AN X-RAY STUDY OF THE INTERNAL STRUCTURE OF CERTAIN CRYSTALS, WITH SPECIAL REFERENCE TO THE COMPLETE STRUCTURAL DETERMINATION OF 4 : 4' - DINITRODIPHENYL $\left[C_{12}H_8(NO_2)_2\right]$ BY THE METHOD OF DOUBLE FOURIER SYNTHESIS.

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J. N. van Niekerk, M.Sc.

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Contents.

This work can be divided into three main parts, the treatment following in the same order as given below.

(p. 18-140) 1) The complete determination of the crystal structure of 4 : 4' - Dinitrodiphenyl $\left[C_{12}H_8(NO_2)_2\right]$. The single crystal rotation method, developed by Schiebold and Polanyi, was used. The method of the Double Fourier Series, first developed by W.L.Bragg in 1929, was used to determine the complete structure. Through the lack of the necessary apparatus no absolute intensity measurements could be made, and as no integrating photometer was available, a scheme had to be devised to express the intensities of all the reflections recorded on the rotation photographs on a relative scale. Intensity measurements represent the fundamental difficulty in this work and limit the accuracy that can be obtained. The structure was projected on two crystal planes, and from the projections the size and shape of the molecules, and the way they pack to form the crystal structure have been determined. $C_{12}H_8(NO_2)_2$ is a complex structure with no symmetry centre. The The crystal can be referred to orthorhombic axes, but structurally it is monoclinic and belongs to the space-group Pc.

(p. 141-149.) 2) The second part of the work deals with the determination of the unit cell of Leucodrin ($C_{15}H_{16}O_8$) and Dibromoleucodrin ($C_{15}H_{14}O_8Br_2$). The space-group of both these organic compounds has been determined uniquely, and is given by the symbol P2,2,2, in the Hermann - Maugin notation. In both cases there are four molecules to the unit cell.

(p. 150-162) 3) The last part of the work gives the determination of the unit cell and space-group of Ammonium-gallifluoride, $(NH_4)_3$ Ga F_6, and outlines a possible structure for this compound. X-ray investigations showed the existence of two impurities in this supposedly pure compound. One of these impurities was identified as Ammonium-Silicafluoride $(NH_4)_2$ Si F_6. The second impurity appears in small quantities as a monoclinic crystal and may be some hydratcd form of $(NH_4)_3$ Ga F_6.

THE CRYSTAL STRUCTURE OF 4 : 4'- DINITRODIPHENYL $(C_{12}H_8(NO_2)_2)$.

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CRYSTAL STRUCTURE BY X - RAY INVESTIGATIONS.

Preliminary Details.

Methods and Apparatus.

The method of the rotating or oscillating crystal, first developed by Schiebold and Polanyi (1), was used during the course of this research. The crystal fragment was placed in a narrow beam of monochromatic X-radiation, and rotated about an axis perpendicular to the X-ray beam while the exposure was taken. The crystal could be given a complete rotation or an oscillation through a limited range. The diffracted beams which flash out when the crystal planes come in a position to reflect were recorded photographically upon a film bent into a cylinder around the axis of rotation. Characteristic $CuK\alpha$ radiation was used, the $CuK\beta$ radiation being partly absorbed by the use of nickel foil. The dimensions of the crystals used seldom exceeded a fraction of a millimeter in any direction, and as a rule the crystals were completely bathed by the incident radiation. With such small crystals the diffracted rays gave small distinct spots on the photographic films. The times of exposure varied from 2 to 8 hours, depending on the size and nature of the crystal under examination and on the output from the X-ray tube. It was only from experience that the most suitable exposures could be established. The X-ray tube was operated at 35,000 volts peak, with a filament current of 3.8 amps, giving and annode output of between 5 and 10 milliamps. Such a low output from the bulb increased the exposures, but it was a necessary precaution to increase the life of the tube as this was the only one of its

(kind)

kind available.

Fig. 1. shows a diagram of the circuit used. The apparatus employed can be regarded as standard for X-ray crystal analysis, and only a brief description will be given. Unrectified supply 220 volts, 50 cycles, was applied to an auto-transformer, the output of which, 130 volts, was applied to the primary of the H.T. transformer. This gave an H.T. output of approximately 35 K.V.peak. The filament transformer input was also 220 volts, 50 cycles, giving an output of approximately 10 volts a.c., with a filament current between 3.8 and 4.0 amps. The output of the bulb as as rule was then between 5 and 10 milli-amps.

W.S. Water control switch.

H. High tension switch.

V. Voltmeter reading to 150 volts.

L. Red lamp.

G. Spark gap.

M.A. Milli-ammeter reading up to 20 m.amps.

A. Ammeter reading to 10 amps a.c.

S.C. Surge coils. These consisted of a few turns of stout wire, to cut out high frequency oscillations which on a few occasions gave rise to heavy sparks in certain parts of the circuit.

The anode and centre part of the tube were electically connected and jointly earthed. The tube was watercooled, the rate of flow being approximately 6 litres of water per minute. The camera, which was also earthed, was placed in close contact with the X-ray tube, the central part of which was kept cool by a fan. For all these experiments a rotation camera was used, the diameter of the cylinder

(containing)

containing the films being 6 cms. With this camera the crystal could be given a complete rotation or an oscillation of 5, 10, or 15 degrees. The camera was complete with collimater and telescope for adjusting purposes, also two arcs at right angles by means of which the crystals could finally be adjusted to rotate about an axis parallel to the axis of the cylinder, and at right angles to the direction of the incident radiation which was in the form of a narrow pencil after passing through the slit system.

Mounting the Crystals.

Only small, single crystals were used. For the purpose of locating single crystals a polarising microscope proved to be very helpful. By examining a collection of crystal specimens under polarised light it was often possible to tell whether any one crystal specimen was single, double, or had some extra bits stuck on to it. A fair idea of the directions of the crystal axes could as a rule be obtained, and very often it was possible to say at once what class the crystal under examination belonged to. An examination of the spots recorded on thr rotation photographs gave final evidence as to whether the crystals under observation were single or complex. Small crystals were mounted with a speck of canada balsam on a sharp point of an ebonite holder which fitted on the rotation camera. For mounting these tiny crystals a binocular microscope of magnification ten was found to be practically indispensable. Under such a microscope the crystal to be mounted was shifted in the required position to the very edge of two glass slides placed one on top of the other. The ebonite holder, with a speck of canada balsam on it, was then carefully shifted along

(until)

until the crystal was touched. If the mounting was not considered satisfactory adjustments could be made by suitable manipulation of the crystal under the binocular microscope or by remounting. The mounting process was a matter of experience and after some time only a few degrees on the arcs of the camera sufficed to accomplish the final adjustments. For reasons to follow it was very useful to mount the crystals in such a way that the two adjustable arcs on the camera gave as nearly as possible independent adjustment to the crystal axes. We shall refer to this as the crystal being mounted with its axes independent. In some cases there were brilliantly reflecting faces round certain zones. The adjustments of the crystal specimens for rotation about such zone axes could be done quickly and accurately by observing the reflected signals from these crystal faces through a telescope fixed to the camera. In the large majority of cases, however, there were no such reflecting faces and the setting of the crystals had to be done by trial. Through experience the necessary adjustments could be made from considerations of the degree of slope of the layer-lines on the trial films. To facilitate these latter adjustments it was found very helpful to have the crystal mounted with its axes independent.

For every photograph taken it was essential to know the direction of the crystal axes with respect to the incident X-ray beam. Where there were good crystal faces developed this could be done accurately by reflection from such faces once they had been identified. In most cases the setting was again done by trial using other properties of the crystal, in particular its external appearance. The final adjustments for the directions of the crystal

(axes)

axes came from considerations of the reciprocal lattice nets. To quote an example we can say that a certain hkl spectrum will just come inside or outside the lunes on the reciprocal lattice net for a certain angle of incidence and rotation of the crystal. The trial film is then indexed to see if these hkl spectra concerned are absent or present as the case may be. In this manner we can make a fairly accurate estimate of the direction of incidence. Great care must be taken not to use spectra for which the structure factors are zero. Such spectra cannot be recorded on the films and may lead to false conclusions if we base our observations on them.

The Reciprocal Lattice and its Applications for Indexing Rotation Photographs.

It was first shown by Ewald (2) that the interference conditions take a very elegant geometrical form when expressed in terms of the reciprocal lattice. The vector to the point (hkl) of the reciprocal lattice is normal to the plane (hkl) of the corresponding crystal lattice, while its magnitude is also the reciprocal of the spacing d(hkl).

In fig. 2. let PO be a vector S_o/λ , that is a vector of length $\frac{1}{\lambda}$ in the direction of the incident radiation wave-normal. Similarly let PQ be S/λ , the corresponding vector in the direction in which the scattering is considered. Suppose PQ is in the direction of a scattering maximum, then it can be shown that PQ must be normal to one of the lattice planes, say to (hkl). The length of OQ is 2 sin θ/λ which, when the diffraction conditions are fulfilled, is equal to $\frac{1}{d(hkl)}$ from Bragg's (3) wellknown reflection law. OQ is therefore in the direction of a vector in the reciprocal lattice and equal to

(it in)

it in magnitude. Thus, if the vector PO is drawn so that O lies at the origin of the reciprocal lattice, Q must lie at another point (hkl) of this lattice. We have therefore the following construction. Let a vector PO of length $\frac{1}{\lambda}$ be drawn in the direction of the incident wave normal, O being the origin of the reciprocal lattice. With P as centre, and radius $\frac{1}{\lambda}$, describe a sphere which of course passes through O. Then the interference conditions are equivalent to the statement that no diffracted beam can arise unless another of the reciprocal lattice points, say Q, lies on this sphere. If it does, then PQ is the direction of the wave normal of a possible diffracted beam. The sphere used in this construction is called the "sphere of reflection" (Ewald's Ausbreitungskugel). The use of the reciprocal lattice construction, in which the consideration of an array of planes is replaced by that of an array of points, is a great simplification in discussing many of the geometrical problems met with in the application of X-ray diffraction.

It is evident from the construction of fig.3. that, for any arbitrary angle of incidence and wavelength, no point of the reciprocal lattice will in general lie on the sphere of reflection, and so no diffracted beam will be produced. By rotating the crystal, and therefore the reciprocal lattice, points may be brought on this sphere, and diffraction can occur. In the rotating crystal method, as the crystal rotates and the reciprocal lattice with it, the reciprocal lattice points pass in turn through the sphere of reflection, and the spectra which flash out as they do so can be recorded on a photographic film.

Each spot on the film represents a spectrum and corresponds to

(a point)

a point on the reciprocal lattice, and the aim in indexing a film is to find which reciprocal lattice point corresponds to a given spot on the photograph. Suppose the rotation of the crystal is about a principal space lattice direction, say a, then the b* and c* axes of the reciprocal lattice lie perpendicular to the axis of rotation. All reciprocal lattice points with the same h index thus lie in a plane perpendicular to the axis of rotation, and give rise to spots on the film on the same layer-line. The zero layer corresponds to $h = 0$, and the first line on either side of it to $h = \pm 1$ and so on. One index of a spot is in this case easily determined, and it remains to determine the other two. Suppose the reciprocal lattice point to be referred not to reciprocal axes, but to cylindrical axes, the axis of rotation being the cylindrical axis. A point is then fixed by co-ordinates ξ, the distance from the axis, ζ the distance parallel to the axis from a plane through the origin at right angles to the axis, and ω the angle which an axial plane containing the point makes with a fixed axial plane taken as reference plane. As the crystal rotates and the reciprocal lattice with it, ω continually changes, but ξ and ζ remain constant. With the rotation of the crystal each point in turn passes through any fixed plane containing the axis, and ξ and ζ are the rectangular co-ordinates of the point at which it passes through the plane. Such an array of points we call a rotation diagram. All the points in a rotation diagram corresponding to rotation about a space lattice axis lie in a series of layer-lines of constant ζ. Since ζ, in the case we have considered of rotation about the a axis is the a* spacing of the reciprocal lattice, we have $\zeta = \gamma_a$ for

(the first)

the first layer-line, $\rho_2 = \frac{2\lambda}{a}$ for the second layer-line, and so on. The values of ρ_2 thus give at once the lattice cell edge parallel to the axis about which the crystal rotates. To get the values of ρ_2 and ξ from the actual photograph is a geometrical problem with a definite solution, and certain graphical methods have been developed which enable us to do it fairly quickly. Charts of this kind have been prepared by Bernal (4) on transparent paper. These charts are superposed on any film taken with a camera of the size for which the charts have been prepared, and by interpolation between the contours the values ρ_2 and ξ for any spot on the film can be read off directly.

Determination of Indices from ρ_2 and ξ

In a complete rotation of the crystal a given set of planes, represented by a reciprocal lattice point and its inverse, intersects any given plane through the axis four times, and will give four spots on the photographic plate. If the rotation is about a zone axis then these four spots will be symmetrically placed around the central point of the photograph. In a complete rotation so many spots are recorded that it is exceedingly difficult, if not impossible, to index the spots from their ρ_2 and ξ values. The indexing can, however, usually be done if only a limited rotation between known angular settings of the crystal is given.

Let us take a definite example as shown in fig. 3. Suppose the crystal to be mounted so that the c axis is the axis of rotation, and let the X-ray beam be incident at right angles to the c axis, and in a plane containing the c and a axes. Suppose an anti-

(clockwise)

anti-clockwise oscillation of 15 degrees to be given to the crystal. Any reciprocal lattice point that passes through the sphere of reflection during this oscillation will give rise to a spectrum unless the corresponding structure factor is zero. The number of spots on any given layer-line which can be recorded is however limited, and they can as a rule be identified without any ambiguity from their ξ values.

The first step in identification is to draw the a* b* net of the reciprocal lattice to some suitable scale. A radius of 20 cms. for the sphere of reflection was found to be most convenient. This according to the convention we have adopted corresponds to ~~this~~ unit length. The sides of the reciprocal lattice net $|a^*| = \frac{\lambda bc \sin\alpha}{\Delta}$ $|b^*| = \frac{\lambda ca \sin\beta}{\Delta}$ are then to be drawn on the scale 20 cms. = 1A, and we construct carefully on a sheet of drawing paper a net having these dimensions. Suppose we are dealing with orthogonal axes then $|a^*| = \frac{1}{a}$ and $|b^*| = \frac{1}{b}$ Consider now the zero layer-line, $\zeta = 0$, for all of whose spots $\ell = 0$. In fig. 3., choosing any point on the reciprocal lattice net as origin 0, from 0 draw a line OP 20 cms. long, the direction of PO relative to the reciprocal lattice axes corresponding to the direction of the incident X-xay beam relative to the crystal axes. With P as centre and radius PO draw a circle passing through 0. This circle represents a trace of the sphere of reflectiom on the plane $c^* = 0$ of the reciprocal lattice. If we consider the lattice net to rotate about 0, in its own plane, the passage of a point through this circle corresponds to the formation of a spectrum. Obviously the same result is attained if we suppose the arc of the circle to be rotated about 0 in its own plane, but in the opposite direction. Let S_2S_2, fig.3.

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be the position of this arc when rotated through15 degrees from its original position S_1S_1'. Then all the lattice points lying within the lunes between the two positions of the circle can give rise to reflection during the 15 degree oscillation. The corresponding spots will be on the zero layer-line of the oscillation photograph. Those in the lune marked L corresponding to spots which lie to the left of the centre, and those in the lune marked R to spots which lie to the right. The distance of any lattice point from O is directly equal to ξ. Thus if the value of ξ for some spot on the film is determined by the Bernal chart, it is usually possible to tell directly from the reciprocal net which of the lattice points corresponds to the reflection; for as a rule there will be only one point within the lune which has the right value of ξ. There may occasionally be some ambiguity when two points within the lune are nearly equidistant from the origin and, if necessary, the decision between the two points can be made by giving the crystal a rotation which will include one but not the other. This was often found to be of great importance in the space-group determinations.

For the higher layer-lines we can proceed in a similar way. The reciprocal lattice points intersect the sphere of reflection now no longer in the equator but in circles of latitude at distances ζ_1, ζ_2 above the equatorial section, and smaller circles must therefore be drawn on the reciprocal net. The radius of these circles can be determined readily if the values of ζ for the different layer-lines are known. This is most simply done by marking off directly on the reciprocal net the shortening of radii for the successive layer-lines. A little consideration is needed in fixing the centres of these circles

(representing)

representing traces of the sphere of reflection on the successive reciprocal lattice layers, and we must distinguish between two cases. 1) When the axis about which the crystal rotates coincides with the corresponding reciprocal lattice axis. This will be the case for orthogonal axes, or for rotation about the b axis of a monoclinic crystal, or the c axis of a hexagonal crystal, the centre of the circles will be the same for all layer-lines, and all that is necessary is to reduce the radii appropriately for the higher ones. 2) When the reciprocal axis does not coincide with the axis of rotation. This occurs when a triclinic crystal is rotated about any zone axis, or when a monoclinic crystal is rotated about the a or c axes. The successive layers of the reciprocal lattice do not then lie exactly one above the other. Each successive layer is shifted relative to the axis, and so relative to the centre of the circle in which this layer intersects the sphere of reflection. In such cases the same net is still used but the origin is shifted by an amount equal to and in a direction opposite to the shift of the successive reciprocal lattice layers relative to the origin, giving us a new direction of incidence. In other words, we change the direction of the incident X-ray beam for each successive reciprocal lattice layer, keeping the reciprocal lattice net fixed.

Calibration of the Camera.

It was necessary to know what degree of accuracy could be expected when making measurements on the films by using Bernal charts. For this purpose a complete rotation photograph of a single NaCl crystal was taken. It was only after many attempts that a suitable small, single NaCl crystal was located. The structure and dimensions of NaCl is known very accurately. Bragg (5) gives a value a = 5.628 A

for this face-centred cubic crystal. Using this value for the cell edges a reciprocal lattice net was carefully constructed.

Certain points of the reciprocal lattice pass through the sphere of reflection, and will give rise to spectra during the complete rotation. These points are evidently those which lie inside the tore which would be obtained by allowing the "sphere of reflection" to make a complete rotation about the same axis with respect to the lattice. It is evident that all possible tores of this kind, corresponding to all possible axes of rotation and angles of incidence, are contained within a sphere of centre 0 and radius 2, using the convention $a.a^* = b.b^* = c.c^* = \lambda$. This sphere is called the "limiting sphere". It contains all the lattice points corresponding to spectra which can, under any circumstances, be obtained from the crystal when using radiation of wavelength λ.

On this net, choosing a suitable origin and paying attention to the direction of the incident X-ray beam with respect to the crystal axes, a circle of radius 40 cms. was drawn passing through the origin. This circle represented a trace of the "limiting sphere" on the plane $\underline{a}^* = 0$ for the crystal rotating about the $\underline{a}$ axis. For the higher layer-lines the necessary modifications as previously described were made. The axes being orthogonal the origin was the same, and it was only necessary to make the appropriate changes in radii for the successive layer-lines.

The ξ values for all the spectra recorded were read off directly using a Bernal chart, and in every case a point (hkl) on this net, corresponding to the value ξ of a spot on the film could be identified. The agreement was satisfactory for in no case did the

(distances)

distances as calculated from the Bernal chart measurements and those measured on the reciprocal net differ by more than 2 mms.

As a further test the spacing of NaCl was determined from this film. A large number of measurements taken at different parts of the film gave a mean value $\frac{s}{2} = .274$.

Hence $a = \frac{\lambda}{\frac{s}{2}} = \frac{1.539}{.274} = 5.62$ A which agrees well with the accepted value of 5.628 A.

THE UNIT CELL AND SPACE - GROUP OF 4 : 4' - DINITRODIPHENYL $\left[C_{12}H_8(NO_2)_2\right]$

Preparation

The crystals of 4 : 4' - Dinitrodiphenyl used in this work were prepared by Dr. W.S.Rapson of the Chemistry Department of the University of Cape Town, who used the method of Gull and Turner (6). Suitable crystals for X-ray examination were obtained by slow evaporation of its solutions in ethyl acetate.

Crystallography.

The crystals so obtained were light amber in colour, and generally took the shape of thin elongated needles or flat plates. In spite of several attempts at recrystallisation it was difficult to obtain good, single crystals free from flaws. In general there were no well defined reflecting faces which made accurate goniometer measurements very difficult. In a few cases these thin, long needles showed the $\{011\}$ prism faces round the zone $[100]$. Goniometer measurements gave the angles between such faces as 63° 32' and 116° 30'. The directions of the crystal faces were chosen so that the angle between the (011) and $(0\bar{1}1)$ faces was 63° 32'. Crystals that developed these prism faces were of very nearly square cross-section, making them suitable for intensity determinations as the path traversed by the X-rays through such crystals was very nearly the same in all directions when the crystal was rotating about the prism axis.

Determination of the Unit Cell.

One of the crystal specimens was mounted about the a axis, which in this case was the long axis of the needle-shaped prism.

(The adjustments)

The adjustments were made by using the method of parallel light reflections from the prism faces until the rotation was accurately about the a axis. The angles between the prism faces {011} were known from previous observations, hence the crystal was set so that the incident X-ray beam was parallel to the b axis. Taking this as the initial direction a 15 degree anticlockwise oscillation was given, allowing an exposure of 4 hours. For rotation about the b and c axes there were no reflecting faces to aid in the preliminary adjustments. Here the method of trial and error was adopted and the final adjustments were made from a consideration of the layer-lines on the trial films. In the latter two cases the direction of the X-rays, relative to the crystal axes, was determined from considerations of the reciprocal lattice net. By considering spectra which could just come on the film, or just not come on, for a certain direction of incidence, say parallel to the a axis for rotation about c, the necessary adjustments could be made and the direction of incidence determined with a fair degree of accuracy.

All these photographs were taken with a Cu-tube, using characteristic Cu kα radiation, The kβ characteristic radiation was partly absorbed by a nickel filter. At a first glance all these photographs showed the presence of faint layer-lines at a distance approximately halfway between the main layer-lines on the films. This apparent halving of the layer-lines suggested a doubling of the spacing in these directions. Closer inspection of the films showed that no such halving existed between the zero and first layer-lines. This led to a careful examination of the radiation from the bulb. The radiation, after passing through a narrow vertical slit system,

(was)

was reflected from the polished surface of a large NaCl crystal and then recorded on a film. The film when examined showed the Cu and Fe spectra, proving that iron was present as an impurity in the bulb. Measurements on the rotation photographs showed that these faint layer-lines were due to Fe kα radiation of wavelength 1.934 A. In later films which were given longer exposures the β peaks of some of the stronger Fe spots could be identified, proving beyond doubt that we were dealing with two types of characteristic radiation. The presence of these Fe spectra called for extreme care when it came to assigning indices to spectra on the zero layer-lines. The Fe spectra could be easily identified and discarded in the higher layer-lines but they often proved troublesome on the zero layer-lines and slowed down the process of identification considerably.

Three films with rotation about the a, b, and c axes were carefully examined in turn with a Bernal chart. The ζ values were accurately measured and the axial lengths determined by substitution in the formula $a = \frac{\lambda}{\zeta_a}$, where λ for Cu kα = 1.539 A. All the spectra lay on both layer- and row-lines. This at once suggested orthogonal axes, the crystal belonging to the orthorhombic class. The size of the unit cell as determined from these measurements is given by

$$a = 3.77 \text{ A}, \quad b = 9.56 \text{ A}, \quad c = 15.39 \text{ A}.$$

Knowing the size and shape of the unit cell it was now possible to calculate the density of this organic compound, and so determine the number of molecules in the unit cell. The molecular weight, on the scale O = 16, of $C_{12}H_8(NO_2)_2 = 244.1$.

(if D is the)

If D is the density in gm/c.c. then

$$D = \frac{1.65 \times 244.1}{3.77 \times 9.56 \times 15.39} \times n \quad \text{gms/cc.}$$

$$= 0.726 \times n \quad \text{gm/cc.}$$

where n is the number of molecules per unit cell. If n = 2, then D = 1.45 gms/cc. This value for the density is in good agreement with the value determined by the method of floatation where D was found to be 1.4 - 1.5 gms/cc.

Rectangular reciprocal lattice nets were drawn for the three films taken with rotation about the a, b, and c axes, special attention being payed to the convention of positive and negative directions of the axes. By the use of Bernal charts these films were now indexed. For every spot recorded on the films there was a corresponding reciprocal lattice point on the nets, and in general the fits were very good even for the highest order spectra recorded. The fact that all these spots recorded were indexed on nets drawn with rectangular reciprocal axes, confirmed the earlier conclusion that the crystal axes were orthogonal. More films were taken with the special aim of bringing in spectra of the form hoo, oko, ool, as some of these spectra did not occur on the films previously taken. These films were again indexed without any ambiguity arising.

A careful survey of the indices assigned to all these spectra revealed that the general reflections hkl of all types occurred, showing that the unit cell having these dimensions was primitive. Reflections hol were present only with l even. There were no other systematic absences. The condition hol absent with l odd is the condition governing a glide plane where, by the operation of such a

(glide plane)

glide plane, there is an apparent halving of the spacing in the c direction. The only symmetry condition then is a glide plane with a glide $^{c}/_{2}$ parallel to the (010) plane.

The Space - Group.

The orthogonal axes of this crystal suggested orthorhombic symmetry. The only symmetry condition found from X-ray analysis was one glide plane, and the unit cell was primitive. This space-group has no place in the orthorhombic class, as is evident when the space-groups given in "Internationale Tabellen zur Bestimmung von Kristallstrukturen, Erster Band" are examined. The existence of one plane implies a second. The space-group Pmc is the only possibility since an X-ray analysis cannot reveal the presence of a mirror plane. This follows from Friedel's Law, which states, that in general the intensities of reflection for (hkl) and ($\bar{h}\bar{k}\bar{l}$) will be identical. This has the effect of adding a centre of inversion to X-ray diffraction photographs.

If we assume this to be the space-group then, with only two molecules to the unit cell, the molecule must sit on this mirror plane. It was necessary now to see how the molecules pack in a unit cell of such dimensions as already determined. The unit cell is only 3.77 A in the a direction. This distance is very nearly the thickness of the benzene ring. The closest approach of neighbouring rings in such compounds as have been investigated is 3.6 to 3.8 A. If we assume these distances of closest approach between neighbouring CH units we must conclude that the molecules must pack with the plane of the benzene rings in, or nearly in, the (100) plane, suggesting this (100) plane as a possible mirror plane. This

(early)

early deduction was later verified from packing considerations.

Solid cardboard models of the molecules were accurately constructed to scale. The dimensions assumed for making the models will be discussed under the heading dealing with the preliminary estimate of the structure (page 30.). When it came to packing two such molecules into the space available, in such a way as to fulfil the condition implied by the glide plane, there were only two possible ways of doing so. We shall consider these two possibilities in turn.

a) The molecules must pack with the "long axis" of the molecules parallel to the c direction of the crystal axes, and with the plane of the benzene rings lying in the (100) crystal planes. We assume here the two benzene rings in the molecule to be co-planar and the long axis of the molecule to be the link between atoms marked C_4 and $\bar{C}_4$ (fig. 12), such a link constituting a common diameter between the two rings. With the molecules disposed of in this manner there was a considerable amount of overlapping of the atoms which could only be overcome by giving the planes of the benzene rings and NO_2 groups a big tilt about this long axis of the molecule. The small spacing in the a direction seems to negative such big tilts. Any such tilts on the benzene rings immediately destroy the possibility of mirror planes if we remember that we already have a glide plane in the space-group and that we can only have two molecules in the unit cell. We must then discard this arrangement as a possible way of packing the molecules.

b) The second possibility was to pack the molecules in such a manner that their long axes made angles of roughly 35 degrees

(with)

with the b axis of the unit cell, assuming the planes of the benzene rings again to lie in the (100) crystal planes. With such an arrangement of the molecules, obeying the space-group conditions, there was only slight overlapping of the atoms which could be done away with by giving the benzene rings or NO_2 groups a small tilt about the long axis of the molecule. This second way of packing the molecules proved to be the more promising and economical as far as space was concerned. If we assume this to be the way in which the molecules pack then it is obvious that only the (100) plane can possibly be a mirror plane. If then the crystal has orthorhombic symmetry the space-group must be Pmc and the (100) plane must be the mirror plane. We shall return to this discussion of orthorhombic symmetry and how the molecules must pack in this case at a later stage.

Refractive Index Determinations.

As an aid in guessing a provisional structure, the three principal refractive indices of the crystal were determined. Crystals used for refractive index determinations came from a fresh deposit and generally took the form of thin, flat plates. Rotation photographs were taken with crystals of this shape, and from these photographs the crystal axes were determined. The axial lengths determined in this way were in very good agreement with the previously determined values of a, b, and c. The a and b directions were found to lie in the flat plane of the crystal plates. Such a collection of crystal plates, lying with their axes in random directions, was exmined under a polarising microscope. Careful examination showed that the crystals showed no

(straight)

straight extinction, a phenomenon which would have been expected if the crystals were structurally orthorhombic. We shall return to this important observation at a later stage.

Small crystals in the form of thin flat plates were immersed in solutions of α - monobromonapthalin and paraffin of different concentrations. For higher refractive indices methylene iodide and sulphur was used giving values up to 1.78. Such crystals, immersed in drops of these refractive index liquids on glass slides, were covered with thin glass slips to give two flat liquid surfaces. They were then examined under a polarising microscope using sodium illumination. The concentration of the solutions was altered until the crystals became nearly invisible in the liquid. The Becke line phenomenon was used as an indication of the direction in which the concentration had to be altered in any given case. It was easy to determine the refractive indices along the a and b directions of vibration since these directions lay in the flat plane of the crystal plates. To determine the refractive index along the c direction one of these flat crystal plates was mounted on the sharp point of a holder with a speck of secotine which was found not to dissolve appreciably in the liquids used. By suitable manipulation of the crystal, completely immersed in the liquid, the refractive index was determined along the c direction of vibration. This was a difficult process and only after numerous attempts were the necessary results obtained. The final results obtained for light vibrating along the three principal directions are given below

$$\alpha = 1.49, \quad \beta > 1.78, \quad \gamma > 1.78.$$

(the values)

The values of β and γ may be much greater than 1.78 which was the highest refractive index of the liquids available. There is sufficient evidence, however, that the crystals are optically negative and very strongly doubly refracting.

We must now return to the very important observation that these crystals do not show straight extinction when examined with polarised light. This observation contradicted the orthorhombic symmetry which was assigned to the structure at a first glance and called for very careful investigation. Such an investigation led to the following important results :

1) The crystals did not show straight extinction when examined under polarised light, and this in itself implied a lower form of symmetry than the apparent orthorhombic symmetry assigned to the crystal at an early stage in this work. A paper by N.F.M.Henry (7) dealing with the subject of non-straight extinction phenomena was referred to. It was found to be irrelevant to the problem under discussion and threw no new light on the subject. The possibility of dealing with complex crystals, or some close form of twinning, was eliminated by first taking rotation photographs of the crystals before examining them under polarised light. In this way it was made certain that we were dealing with single crystals only.

2) A closer examination of the rotation photographs showed that in some cases there was a marked difference in the intensity of corresponding spots coming on corresponding positive and negative layer-lines. This was only true for films taken with the rotation about the a and c axes. All films taken about the b axis were perfectly

(symmetrical)

symmetrical about the zero layer-line. This important observation was overlooked at the outset where we were mainly concerned with the distance apart of the layer-lines and with assigning indices to the spectra recorded. From these observations it followed then that the intensities of the general hkl and $\bar{h}kl$ spectra were different. Also hkl and $hk\bar{l}$ differed in intensity, whereas hkl and $h\bar{k}l$ were equal. All these observations were done visually but they were quite reliable and pointed quite definitely against orthorhombic symmetry.

3) If the crystal had orthorhombic symmetry then, as has been pointed out already, the space-group can only be Pmc. From packing considerations it followed that the (100) plane must then be a mirror plane. Two cases now arise and we shall consider these in turn. a) Since there are only two molecules in the unit cell and we already have a glide plane in the space-group, the molecules must pack with all the C and N atoms lying in this (100) mirror plane, with the plane containing the oxygen atoms in the NO_2 group at right angles to the mirror plane. A little consideration will show at once that such an arrangement of the molecules is impossible. The O - O distance in the NO_2 group as determined by James King and Horrocks (8) for para- dinitrobenzene is 2.14 A. Bragg (9) gives a value 1.32 A for the ionic radius of oxygen. If we assume similar distances in this structure then it is at once clear that space does not allow the molecules to pack in the above mentioned way. Such an arrangement would require the a axis to be at least (2.14 + 2.64) = 4.78 A, a value considerably greater than the value 3.77 A already determined. b) The molecules must pack with all the atoms

(in the)

in the (100) plane. Previous considerations showed that with such an arrangement there was slight overlapping of the atoms, suggesting a small tilt of the benzene rings or NO_2 groups. Such a small tilt would immediately rule out any mirror planes. From purely packing considerations then it does not seem possible to pack the molecules in this manner. Secondly, and more important, if all the atoms lie in this (100) plane they will all scatter in phase along the a direction. With such an arrangement we should then expect very strong low order hoo spectra, the intensity falling off in a regular way for the higher hoo orders. A mere visual comparison showed that the 100 spectrum was weak when compared with some of the stronger spectra recorded, whereas on this assumption it should have been the strongest spectrum recorded. Also 200 was found to be completely absent, and 300 came as a weak spot on the film. These observations on intensities ruled out such an arrangement of the molecules.

4) At a later stage in this work a Fourier synthesis was made which involved the relative intensity measurements of all spectra of the form hol. It was found that hol and $\bar{h}$ol differed very greatly in intensity, and we should expect these to be the same if the crystal were structurally orthorhombic. These relative intensity measurements of the hol planes completely confirmed the conclusions arrived at previously.

Taking all these facts into consideration we must conclude that the crystal cannot have orthorhombic symmetry. The elimination of any possible orthorhombic symmetry fixes the space-group as C_s^2 or Pc in the Hermann-Maugin notation, the crystal belonging to the Monoclinic Hemiedric class.

(the existence)

PRELIMINARY ESTIMATE OF THE STRUCTURE.

Sources of Information.

In deciding what is the probable structure of the crystal, we may use first our knowledge of the optical properties, and secondly the information as to the size and shape of the benzene ring that has been provided by the work of Mrs. Lonsdale (10) Robertson (11) and others. The crystal has two large refractive indices, which we can consider to be roughly of the same order, and one smaller refractive index. From this we can infer that the directions of vibration, b and c , for the two large refractive indices are nearly parallel to the plane of the benzene rings, the third direction then being nearly at right angles to the plane of the rings.

The benzene ring is known to approximate very closely to a regular hexagon of edge 1.4 A, and the closest approach of neighbouring rings in such compounds as have been investigated is 3.6 to 3.8 A. Dhar (12) gives a value 1.48 for the C - C link between rings in diphenyl. We shall assume this link to be parallel to the common diameter line of the two rings and further assume the two benzene rings in the molecule to be co-planar. These seem reasonable assumptions to make at this stage of the analysis. The size and shape of the nitro group, and the distance C - N, were assumed from values obtained by James, King and Horrocks (8) in determining the structure of para-dinitrobenzene. Using these dimensions, solid cardboard models of the molecules were constructed to scale. When it came to packing two such models into the unit cell in such a way as to fulfil the symmetry conditions and to satisfy the demands of the refractive

(indices)

indices, very little space was available.

Preliminary assumed Structure.

Assuming the carbon and nitrogen atoms all to lie in the (100) crystal planes, the molecules could only be packed if their long axes, or the C - C links between rings, made an angle of approximately 35 degrees with the b axis, and if the line joining O - O in the nitro group was inclined at an angle of roughly 25 degrees to the plane of the benzene rings which, on our assumption, is also the (100) crystal plane. Such a twist of 25 degrees of the NO_2 groups is necessary to overcome overlapping of the atoms. The type of arrangement to which this reasoning leads may be seen from fig. 12, which represents the projection of the final structure on the bc plane. More detailed work based on intensity measurements shows these preliminary ideas to be very near the truth.

If this provisional structure was near the true structure it promised clear resolution of the atoms in the bc plane. Accordingly it was decided to carry out a two-dimensional Fourier synthesis of the electron density projected on the bc plane, viewed parallel to the a axis.

FOURIER SYNTHESIS AND ITS APPLICATION TO CRYSTAL STRUCTURES.

Without assuming any symmetry in the density distribution, the nature of a crystal requires the structure to be periodic over a range defined by the primitive translations, a, b, c, of the unit cell, and hence the density, $\rho(xyz)$, can be represented by means of a triple Fourier series. The use of a Fourier series to represent the results of X-ray analysis was first suggested by Sir William Bragg (13) in 1915, and developed by Duane (14), Havighurst (15) Compton (16) and others. The Fourier series that represents the electron density (number of electrons per unit volume) at any point (xyz) is given by the expresssion

$$\rho(xyz) = \frac{1}{V}\sum_{-\infty}^{+\infty}\sum_{-\infty}^{+\infty}\sum_{-\infty}^{+\infty} F(hkl)\, e^{2\pi i\left(\frac{hx}{a}+\frac{ky}{b}+lz/c\right)} \quad \ldots\ldots (1)$$

where V is the volume of the unit cell, a, b, c the translations.

It is important to note that F(hkl) for any given plane is in general a complex quantity, characterised by an amplitude and a phase constant. Experimental measurements of intensities determine the moduli of the structure factors, $|F(hkl)|$, but give no information regarding the relative phase relationships. The different reflections are measured at different times, with the crystal in different positions and so all information regarding the phase relationships is necessarily lost in making the experiment. This question of phase relationship represents the fundamental difficulty in X-ray analysis, and in the general case the problem of determining the density, $\rho(xyz)$, from intensity measurements cannot be solved.

The constant term in the above expression, for which h = k = l = 0, is equal to Zo, the total number of electrons in the unit cell of

volume V. We may think of F(ooo) as characteristic of a spectrum of zero order, or radiation scattered in the direction of the transmitted beam. Expression (1) above suggests the possibility of a direct method of crystal analysis. If the values F(hkl) are measured for a large number of reflections, then the density throughout the crystal can be calculated by means of a Fourier series, and the centres of the atoms will be shown as positions of large density. X-ray measurements give the amplitudes but not the phases of the diffracted beams. This lack of knowledge of the phases makes the Fourier method very difficult except in the case of crystals with a centre of symmetry. All the Fourier terms must be a maximum or a minimum at such a centre of symmetry, hence all values of F(hkl) must be real when such a symmetry centre is used as origin. The question of sign still remains, but this can often be settled by a preliminary analysis of the structure using considerations other than optical which, as a rule, will give one sign or the other.

Such a triple Fourier series is difficult to handle, and involves an enormous number of terms. The method of the Double Fourier series, developed by W.L.Bragg (17) in 1929, is much more useful in practice, far fewer terms are involved, and the calculations can be handled quite easily. If all the reflections around a crystal zone are measured, and a double series formed, it gives the projected electron density per unit area on a suitable plane, viewed parallel to a chosen direction. If the electron density is calculated at a number of points over the projection, then by joining points of

(equal)

equal density the contour diagram so obtained will give a graphical representation of the results. Atoms are then shown as peaks surrounded by more or less concentric circles.

To evaluate the Fourier series the Fourier coefficients, given by F(hkl), must be determined. In the case of a small crystal element of volume αV, so small that its absorption of the incident X-ray beam is not appreciable, the following expression for the integrated reflection can be calculated

$$\frac{E\omega}{I_0} = \left[N \frac{e^2}{mc^2} F(hkl) \right]^2 \lambda^3 \times \frac{1+\cos^2 2\theta}{2 \sin\theta} \alpha V \quad \ldots (2)$$

where N is the number of unit cells per unit volume of the crystal, and $\frac{1+\cos^2 2\theta}{2}$ a polarisation factor calculated on the assumption that the incident beam is unpolarised as is usually the case when characteristic radiation is used. E is the total energy reflected when the crystal rotates with constant angular velocity ω through the reflecting position, and I_0 the intensity per unit area of the incident radiation. For any given direction θ that the incident beam makes with the (hkl) crystal planes, the square of the modulus of the corresponding structure factor, $|F(hkl)|^2$, is proportional to the integrated reflection, a quantity which can be determined experimentally.

In the case of a crystal with a centre of symmetry we can then determine the values of $|F(hkl)|$ experimentally. If such a symmetry centre is taken as origin the values of F(hkl) must be real. The question of sign must as a first approximation be determined from properties other than optical such as packing considerations,

(refractive)

refractive indices etc. A preliminary projection of the structure, using only the higher Fourier coefficients, will in general lead to results nearer the truth. In this manner, by a series of successive approximations, the true structure can be derived at.

In the case under examination of a crystal without a centre of symmetry the phase angles must be determined from the calculated values of F(hkl), using an assumed probable structure, and then combined with the experimentally determined values of these structure factors. The exact procedure that was followed will be described briefly under the heading Fourier series and its Evaluation (page 81). We have seen that in the general case F(hkl) is a complex quantity, characterised by an amplitude and a phase constant, and experiment can only determine $|F(hkl)|$. If $Fe^{-i\delta}$ represents any complex quantity we can put it in the form

$$Fe^{-i\delta} = F\cos\delta - iF\sin\delta$$

$$A - iB$$

Hence $|Fe^{-i\delta}| = \sqrt{A^2+B^2}$, and $\delta = \tan^{-1} B/A$

where $A = F\cos\delta$ and $B = F\sin\delta$

Going back to equation 1) we can put our structure factor in the form

$$|F(hkl)| = \left[\sum A^2 + \sum B^2\right]^{\frac{1}{2}}$$

where $\delta = \tan^{-1} \frac{\sum B}{\sum A}$

$$A = fo \sum \cos 2\pi\left(\frac{hx}{a}+\frac{ky}{b}+lz/c\right)$$

$$B = fo \sum \sin 2\pi\left(\frac{hx}{a}+\frac{ky}{b}+lz/c\right).$$

the summation being understood to extend over all the equivalent points in the unit cell, and fo being the atomic scattering factor

(appropriate)

appropriate to the plane (hkl).

It was desirable to make a Fourier projection on the bc plane viewed parallel to a, as the provisional structure promised clear resolution of the atoms on this plane. We must then confine the series to two dimensions and express the density per unit area by

$$\rho(yz) = \frac{1}{A} \sum_{-\infty}^{+\infty} \sum_{-\infty}^{+\infty} F(okl)\, e^{-2\pi i\left(\frac{ky}{b} + lz/c\right)}$$

where A represents the area of the cell face upon which the projection is made.

To our knowledge only one other example of a crystal without a centre of symmetry has been worked out. This was done by Robertson (18) when determining the structure of resorcinol. Reference to this paper and another one by Robertson (19) which deals with structures having no centres of symmetry, gave some very useful hints when the projection of the crystal under examination was started.

INTENSITY DETERMINATION.

Scheme for measuring Relative Intensities.

To evaluate the series for $\rho(yz)$ it was necessary to determine the structure factors F(okl), for all the spectra having indices of the type okl arising from crystal planes belonging to the zone [100]. The limitation of not being able to make absolute intensity measurements, through the lack of the necessary apparatus, was realised at an early stage. The great advantage of making such absolute intensity determinations will be discussed fully in a later section of this work. No integrating photometer was available for measuring the integrated reflections of the spectra recorded on the rotation photographs. A scheme had to be worked out to measure the relative intensities of all the spectra round this zone as accurately as possible.

After many attempts a suitable crystal was finally cut and mounted about the a axis, ready to determine the necessary okl spectra. The length of this crystal specimen in the a direction was approximately 0.3 mms. It was of very nearly square cross-section, the dimensions along the b and c directions being just under 0.2 mms. Extreme care was exercised in making the necessary adjustments, until the layer-lines on the trial films were perfectly straight when the crystal rotated about the a axis. The direction of the incident

(X-ray beam)

X-ray beam, relative to the crystal axess, was accurately determined by the method of reflection from the prism faces. This direction was finally checked by using the reciprocal lattice net. The trial films showed that exposures of four hours were suitable for the conditions under which the bulb was operated. Observations showed that with the crystal fragment in position on the camera it was completely bathed in the incident X-ray beam during the exposures.

For the first intensity photograph the X-ray beam was parallel to the b axis of the crystal. The vernier reading on the camera was recorded, and an anticlockwise oscillation of15 degrees given to the crystal. For the next film the crystal was turned through an angle of 10 degrees anticlockwise and a similar oscillation and exposure given. In this way it was insured that certain spectra were common to each pair of successive films. Using these common spectra one film could now be standardised in terms of the other. This was a necessary precaution because spectra on two successive films were not recorded under the same conditions as is evident from the following reasons. a) It was impossible always to put the camera back in the same position, hence the position of the crystal relative to the incident radiation may vary slightly. These slight variations may, however, cause serious differences in the intensity of corresponding diffracted beams. b) The electrical circuit could not be adjusted so that the bulb gave the same power output from day to day. c) The conditions under which the films were developed varied from time to time. d) Finally two films need not necessarily have the same sensitivity and protection against scattered white radiation.

In this way, with successive 10 degrees rotations, a set of 18

(FILMS)

films was taken covering the whole 180 degrees round this zone axis. By the usual Bernal chart method indices were assigned to all the spectra coming on the zero-layer lines, as these were the only spectra concerned for this projection.

The next problem was to make relative measurements of all the 0K1 spectra. This was done by measuring the density (amount of blackening) of the spots on these rotation photographs with a microphotometer. The film was fixed to a carriage mounted on rails and driven by clockwork. This carriage moved very slowly in front of a narrow, vertical beam of light, focussed on the narrow circular aperture of a photoelectric cell arrangement. The photoelectric cell was connected to a very sensitive Moll galvanometer which threw a beam of light on the revolving drum, driven by the same clockwork as the carriage. The film was adjusted very carefully until the centre of the spots on the zero layer-line passed accurately through the centre of the photoelectric cell aperture when the carriage was slowly driven along in front of the source of illumination. This adjustment could only be accomplished if the layer-lines were perfectly straight, which in turn implied a very accurate setting of the crystal. The source of illumination was kept steady throughout all these observations. As the film was slowly pulled along, spectra on the zero layer-line passed in turn through the light beam focussed on the photoelectric cell. The fluctuations in the density of the spots caused irregular kicks in the Moll galvanometer. These kicks were recorded as a continuous trace on a film wrapped round the revolving drum. By means of a shutter arrangement the "zero line" on all such traces was determined. This "zero line" is the horizontal trace obtained (when)

when no illumination falls on the photoelectric cell.

Figure 4. shows such a specimen trace, or photometer curve.Each peak on the photometer curve corresponds to a definite spectrum on the corresponding rotation photograph. These peaks were given their proper indices. The simplest way of doing this was graphically. The values in Bernal units, of spectra on any X-ray film were plotted against the distance in cms. of the peaks on the corresponding photometer film measured from the centre of the film. A few peaks, due to prominent X-ray spectra, can always be easily identified and the graph plotted. Using this graph the peaks on all the photometer films could then be readily identified, as the values for all the spectra were already known.

Determination of intensity curve. The next important step was to assign intensities, on an arbitrary scale, to all the peaks recorded on the photometer curves. A segment disc, maximum radius 7 cms., of 12 equal segments, the radius of adjacent segments differing by 0.5 cms., was constructed out of thick brass. The disc fig. 5.,was made to rotate rapidly infront of a film holder, placed at a distance of about 2 metres from the X-ray tube, where the radiation was assumed to be uniform over a wide area. The film inside the holder was protected by a thick slab of lead with which it was in close contact. A rectangular slit 8 cms. long and 0.5 cms wide was made in this lead slab, so that only this portion of the film was exposed to the incident X-radiation. The disc was adjusted so that the top portion of the narrow strip of film was always exposed to the radiation, when the disc was rotating closely in front of the lead slit. The lower portion of the film was always completely shielded)

shielded from the X-radiation. With such an arrangement, shown in plan in fig. 5., a series of steps, increasing in density, was obtained when the film was devloped, the time of exposure for each step being accurately known.

After many trials satisfactory exposure conditions were finally obtained. Two such film strips, exposed for 2 and 4 minutes respectively, were taken side by side on the same piece of film under the same conditions. The X-rays were screened off for a short time, while the film was shifted in position for the second exposure, thus ensuring uniform radiation for both exposures. Also the two strips were taken on the same film, hence the conditions of developing were the same.

Photometer curves were taken of the two film strips finally obtained, care being taken to get the zero line in each case, and to keep the conditions as far as possible the same. The curves so obtained approached the zero line in a series of steps, the increase in height of successive steps decreasing for increasing exposures. Such a photometer trace is shown in fig. 6., showing two curves P and Q for different exposures and illustrating the meaning of the measurements h_o and h for any one step. Each step on this photometer trace corresponds to a definite and known time of exposure, the distance h_o corresponding to zero exposure. The distance h was accurately measured for each step, and the value (h_o-h)cms. calculated. A graph of (h_o-h) in cms. was plotted against the time of exposure in seconds.

While making this experiment it was found necessary to adjust conditions so that the highest step, corresponding to the largest

(exposure)

exposure, did not approach the zero line too closely, and so make the corresponding distance h too small to be measured accurately. Such conditions could only be achieved by constant a trial, varying the time of exposure, and the distance from the source of radiation. It was advisable to make the time of exposure so long, that a possible extra revolution of some segment of the disc would not seriously affect the intensities recorded. In other words the number of revolutions during the time of exposure must be large. The distance between film and source of radiation could always be altered to give the desired conditions.

Measurements on the two final photometer curves so obtained are given in the table to follow.

Curve I (Exposure 4 min.)

Steps	ho cms.	h cms.	ho-h cms.	I sec.
1	7.10	4.30	2.80	20
2		3.50	4.60	40
3		1.50	5.60	60
4		0.86	6.24	80
5		0.60	6.50	100
6		0.43	6.67	120
7		0.32	6.78	140
8		0.24	6.86	160
9		0.20	6.90	180
10		0.18	6.92	200
11		0.16	6.94	220
12		0.13	6.97	240

Curve 2. (Exposure 2 min.)

Steps	ho cms.	h cms.	ho-h cms.	I sec.
1	7.10	5.55	1.55	10
2		4.04	3.06	20
3		3.09	4.01	30
4		2.38	4.72	40
5		1.92	5.18	50
6		1.52	5.58	60
7		1.25	5.85	70
8		1.08	6.01	80
9		0.90	6.20	90
10		0.77	6.33	100
11		0.66	6.44	110
12		0.55	6.55	120

Using these values a mean curve, shown in fig. 7., was drawn of (h_o-h) against I. Circles and crosses show the points obtained from curves I and 2 respectively. We shall refer to this as our Intensity Curve.

If conditions were perfect then these two graphs should coincide. The discrepancies found may be due to a number of factors such as a) Fluctuations in the intensity of the X-radiation. b) Unavoidable small errors in timing. c) Possible variations in the light intensity when using the microphotometer. d) Rotation of the sector disc so that a portion of the film may be exposed for, say 274 revolutions, whereas 275 revolutions determine the exposure of the rest of the film. This latter reason together with the timing were probably the main causes. Numerous attempts were made, without success, to establish complete coincidence between the two curves. The graph in fig. 7. shows the closest approach to coincidence between two independent curves.

Intensity Curve Applications. This Intensity Curve, determined experimentally, was used for determining the intensity of the spots on the X-ray photographs in terms of seconds of exposure. The photometer curves showed a continuous trace of the background on the corresponding X-ray films, the spectra on the films being indicated by steep peaks rising above the background trace. This background trace on the photometer curves was extended as a continuous curve running through the bases of the peaks. Experience showed how to extend this continuous background trace for strong low order spectra, which sometimes came close in on heavy streaks. In such cases the background was often very high and a little consideration was (necessary,)

whereas for the higher order spectra it was a simple matter to extend the continuous background trace. The values h_o and h were accurately measured for every peak that represented a definite spectrum. All measurements were made from the zero line, h being the distance to the top of the peak and h_o the distance to the background on which the peak ocurred. From the Intensity Curve the values ho and h were determined in terms of seconds of exposure.The value (h - ho) sec. then gives the intensity of any peak on this scale of measurement. In this way a certain value of intensity, expressed in seconds of exposure, was determined for every OKl spectrum recorded, except for those spectra that were overexposed. Such spectra will be dealt with at a later stage.

Spectra recorded on separate films were not subjected to the same conditions, so that the values of intensity calculated for certain OKl spectra ocurring on one film, may be totally different from those calculated for the corresponding OKl spectra coming on the next film. It was necessary then to bring all these intensity measurements to the same scale, thus giving a relative estimate of the intensities of all the spectra recorded. We may call this process the standardising of all the films in terms of one particular film chosen as standard. This process of standardising was done in two stages:

1)Careful examination of the intensities observed so far showed that the intensities of spectra OKl and $O\bar{K}l$ would agree well, but for the fact that they were not expressed on the same scale. In other words the intensities of OKl and $O\bar{K}l$ were the same, as was to be expected for a monoclinic crystal. Films were taken at 10 degree

(intervals)

intervals through 180 degrees and there were always two corresponding films with very nearly the same set of spectra on them, only if spectra okl occur on the L.H.S. of one film they occur on the R.H.S. of the corresponding film. Taking the films in pairs, corresponding films were expressed on the same scale of intensity simply by multiplying all the intensity values on one film by a calculated factor.

2. The films were now standardised in pairs, and it was necessary to standardise all such pairs in terms of one particular pair chosen as standard. Suppose A, A' and B, B' are two such pairs that have been standardised. Suppose also A and B are two successive films taken at a 10 degree interval. The oscillation given was 15 degrees, and so A and B will have some spectra in common. Similarly A' and B' will have some common spectra. From these common spectra a mean factor can be calculated, and the two pairs A, A' and B, B' brought to the same scale. Any one film, with a fair intensity distribution of spectra on it, was chosen as standard, and in the way described above the intensities of the spectra on the rest of the films were expressed in terms of these standard values. Such 10 degree intervals between successive photographs gave a fair number of common spectra so that a reasonable mean factor could be calculated for standardising one such pair of corresponding films with the next.

Choosing one such pair of corresponding films out of a set of nine an illustration is given to show

a) How the intensities were determined from the photometer peaks,

b) How such a pair of corresponding films was standardised,

(c)

c) The calculation of the mean factor for standardising one such pair of corresponding films with the next. In the illustration that follows films marked F20 and F21 were such a pair of corresponding films for which a mean factor F was calculated to express the intensities on the two films on the same scale.

F 20 L.H.S.

Index	ho cms.	h cms.	ho sec.	h sec.	(h-ho) sec.	(h-ho) × 1.56 sec.
$0\bar{2}1$	-	-	-	-	v.strong	v.strong
$*0\bar{3}2 + \beta$	2.38	0.31	41	146	105	164
$0\bar{4}3$	-	-	-	-	v.strong	v.strong
$0\bar{4}4$	2.30	0.29	42	149	107	167
$*0\bar{5}4$ just in	3.50	2.92	26	33	7	11
$0\bar{5}5$	3.89	0.82	22	89	67	104.5
$0\bar{5}6$	4.07	2.64	21	37	16	25
$0\bar{5}7$	4.45	4.10	18	20	2	3
$0\bar{6}7$	4.73	4.19	16	20	4	6
$0\bar{5}9$	4.73	3.74	16	24	8	12.5
$0\bar{5}10$	4.80	4.05	16	21	5	8
$0\bar{5}11$	4.88	4.30	15	19	4	6
$0\bar{5}12$	4.85	4.00	15	21	6	9.4
$0\bar{5}13$	4.78	2.70	16	36	20	31
$*0\bar{5}14$ just in	4.75	4.43	16	18	2	3
$0\bar{6}13$	4.77	4.30	16	19	3	4.7

Index	F 20. L.H.S.	F 21. R.H.S.	$\frac{F\ 21}{F\ 20}$
044	107	179	1.67
055	67	104	1.55
056	16	26	1.63
067	4	7	1.75
059	8	12	1.50
0510	5	8	1.60
0512	6	10	1.67
0513	20	27	1.35
o511	4	7	1.75
0613	3	5	1.67

Mean $\frac{F\ 21}{F\ 20}$ = 1.61

* such spectra were discarded as being uncertain.

Factor for standardising F 20 in terms of F 21

$$F = \frac{1.61 + 1.50}{2} = 1.56$$

F 21. R.M.S.

Index	ho cms.	h cms.	ho sec.	h sec.	(h-ho) sec.
021	-	-	-	-	strong
031	4.10	2.80	20	34	14
032	4.20	0.52	19	113	94
042	3.70	0.42	24	126	102
043	-	-	-	-	strong
044	3.50	0.17	26	205	179
054	4.60	2.20	17	44	27
055	5.10	0.49	13	117	104
056	5.60	2.64	10	36	26
057	-	-	-	-	-
*058 or 066	6.12	4. 17	8	20	12
067	6.23	5.22	6	13	7
059	6.28	4.40	6	18	12
068	6.30	5.72	6	9	3
0510	6.30	5.04	6	14	8
0511	6.31	5.40	5	12	7
0512	6.23	4.77	6	16	10
0513	6.03	2.82	7	34	27
0514	5.80	5.20	9	13	4
063	5.80	5.00	9	14	5

F 20. R.H.S.

Index	ho cms.	h cms.	ho sec.	h sec.	(h-ho) sec.	(h-ho)×1.56 sec.
010	2.10	0.60	46	91	45	70
020	-	-	-	-	v.strong	v.strong
031	3.35	2.54	27	38	11	17
041	3.58	2.02	25	47	22	34.3
042	3.60	0.60	25	106	81	126.4
052	3.75	2.92	23	32	9	14
053	3.68	2.43	24	40	16	25
054	3.68	2.06	24	47	23	36
064	4.35	3.30	18	28	10	15.6
065	4.51	4.02	17	21	4	6
066	4.65	3.73	17	24	7	11
067	4.75	4.20	16	20	4	6

Index	F 20. R.H.S.	F 21. L.H.S.	$\frac{F\ 21}{F\ 20}$
010	45	72	1.60
031	11	16	1.45
041	22	32	1.45
042	81	125	1.54
053	16	20	?
054	23	33	1.44
064	10	13	1.30
066	7	10	1.43
067	4	7	1.75

Mean $\frac{F\ 21}{F\ 20} = 1.50$

F 21 L.M.S.

Index	ho cms.	h cms.	ho sec.	h sec.	(h-ho) sec.
$0\bar{1}0$	2.30	0.52	42	114	72
$0\bar{2}0$	-	-	-	-	strong
$0\bar{3}1$	4.50	2.84	17	33	16
$0\bar{4}1$	4.70	2.00	16	48	32
$0\bar{4}2$	4.60	0.32	17	142	125
*$0\bar{4}3$ just in	4.30	2.81	19	34	15
$0\bar{5}3$	4.10	2.39	20	40	20
$0\bar{5}4$	4.50	1.91	17	50	33
*$0\bar{5}5$ just in	5.20	1.30	13	67	54
$0\bar{6}4$	5.40	3.63	12	25	13
*$0\bar{6}5$ just in	5.60	4.80	10	15	5
$0\bar{6}6$ ~~5.78~~	5.78	4.23	9	19	10
$0\bar{6}7$	5.98	4.80	8	15	7
$0\bar{6}8$	6.04	5.70	7	10	3
*$0\bar{6}9$ or $0\bar{7}7$	6.10	5.32	7	12	5

The values in the last column represent the intensities of these spectra, all expressed on the same scale. In a similar way the other pairs of corresponding films were standardised one in terms of the other.

These corresponding pairs must now be expressed on the same scale. To do this any one pair was taken as the standard. In the case under consideration films 19, 20 and 21, 22 were successive films which had certain spectra in common. Films 19 and22 were such a pair of corresponding films which had already been standardised. To save space the values for 19 and 22 are not given here, only tables giving the values of common spectra are given.

Index	F 19	F 20	$\frac{F\ 20}{F\ 19}$
064	12	15.6	1.30
044	128	167	1.31
057	2	3	1.50
059	11	12.5	1.14
041	27	34	1.26

Mean $\frac{F\ 20}{F\ 19} = \underline{1.30}$

Index	F 22	F 21	$\frac{F21}{F22}$
064	9	13	1.44
032	79	94	1.19
044	149	179	1.20
059	10	12	1.20
0513	22	27	1.23

Mean $\frac{F\ 21}{F\ 22} = \underline{1.25}$

Mean factor $F = \frac{1.30 + 1.25}{2} = 1.28$

F here is the mean factor between corresponding pairs F 20, F 21. and F 19, 22. If all the intensity values of F 19 and F 22 are now multiplied by this factor, then the values on F 19, 20, 21, 22 will

(all be)

all be expressed on the same scale, the initial values on F 21 being taken as a standard of measurement. Following a similar treatment all spectra recorded on this set of intensity ~~values~~ films were expressed on the same scale.

Very often two points on the reciprocal lattice net were very nearly equidistant from the origin, (eg. 058, 066 and $0\bar{6}9$, $0\bar{7}7$ on the films illustrated.) and measurements on the reciprocal lattice net made it difficult to decide in favour of any one spectrum. Fortunately this was not a frequent occurrence, and such spectra were usually separated on the next film taken, the position of the lines on the reciprocal lattice net making it impossible for one of them to occur. If there was any doubt, it was a comparatively simple matter to calculate the setting of the crystal such that only one of these doubtful spectra could occur when a rotation of 5, 10, or 15 degrees was given to the crystal.

When making these intensity observations it was found that a number of low order spectra were overexposed, thus making their intensity determinations impossible from the films taken. As a rule any peaks on the photometer curves that approached the zero line to within a distance $h < 0.2$ cms., corresponding roughly to an exposure greater than 180 seconds not taking background into consideration, were regarded as overexposed, and a redetermination of their intensities made. The crystal was set so that these strong spectra, together with other spectra of determined intensities were recorded. The exposure was so arranged that these strong spectra appeared as dark spots but not overexposed. Comparing the intensity values of such spectra and those previously determined, the intensities

(could)

could all be expressed on the same scale. As a rule the necessary factors for this latter standardisation had values ranging between 4 and 6. In a few cases where the intensities were high, such as for the 012, 013, 022 spectra, the value of this standardisation factor was as high as 16.

In this manner relative intensity values were found for all the spectra recorded round this zone. Inspection showed that within the errors of experiment 0K1, 0K̄1, 0KĪ and 0K̄Ī all had the same intensity values. On the average the intensity of every 0K1 spectrum was given by six independent determinations. The agreement between these independent values was satisfactory if experimental difficulties and the unavoidable errors during the process of standardisation were taken into account. The mean of all these values for a certain 0K1 spectrum was taken to represent the final intensity of that spectrum.

It must be pointed out at this stage that the way of arriving at, and expressing these intensity values is purely arbitrary, the intensity values having no real meaning in the true sense of the word. What was measured was the density of a strip of constant width, governed by the area of the circular aperture in front of the photoelectric cell, across the centres of the spots on the rotation photographs. The densities of such strips were presumably proportional to the areas under the photometer peaks. What we measured was the height of these peaks which in turn is related to the area under the peaks. We can say that these heights represent the maximum density of the spots recorded, and is in some way related to the total density of the strips across these spots. As already pointed out the peaks measured never approached the zero line on the photometer traces too

(closely)

closely, If this was the case a redetermination of such peaks was made giving a shorter exposure. In other words,all the density maxima measured, given by the height of the peaks, were of the same order and can accordingly be taken to give a measure of the relative density maxima. When determining the integrated reflection, the whole area of the spots is taken into account, instead of strips across the centre of the spots as in our case. It seems reasonable to assume that the density of such strips across the centre of the spots must be related to the density given by the entire area of the spots. Now the density of these spots is related to the intensity of the reflected beams giving rise to such spots on the photographic film. It appears then that the intensities we have measured are related in some way to the integrated reflections, but exactly what this relation is, will be hard to say.Throughout these observations the results were always consistent, strong spectra always giving dark spots and hence high peaks, which again led to high intensity values. It seems reasonable to assume then that the intensity measurements made gave the same order of rising and falling off of intensity , as would have been given if absolute intensity determinations had been made, and that our relative values for the intensities gave a far better representation than a mere visual comparison of spectra on the films.

The following table gives the values of the final intensities I, expressed in seconds of exposure, for all the okl spectra observed.

Index	I	Index	I	Index	I	Index	I
002	282	0110	15	037	44	054	24
004	92	0111	19	038	7	055	78
006	300	0112	-	039	10	056	21
008	404	0113	3	0310	5	057	2.5
0010	20	0114	-	0311	15	058	3
0012	-	0115	-	0312	7	059	10
0014	12	021	212	0313	25	0510	6
010	54.0	022	380	041	26	0511	5
020	331.2	023	300	042	85	0512	8
030	18.0	024	162	043	509	0513	22
040	5.4	025	192	044	130	061	12
050	6.6						
060	15.0	026	25	045	69	062	17
070	-	027	10	046	5	063	3
080	121.2	028	22	047	4	064	10
011	32	029	8	048	7	065	5
012	1232	0210	5	049	29	066	8
013	780	0211	5	0410	14	067	5
014	66	0212	-	0411	125	068	2
015	7	031	12	0412	11	069	-
016	6	032	70	0413	15	071	-
017	9	033	195	051	18	072	3
018	27	034	20	052	6	073	16
019	5	036	100	053	16	081	-
		035	45			082	13
						083	3.

STRUCTURE FACTOR CALCULATIONS.

The crystal is monoclinic and belongs to the space-group Pc. The (010) plane is a glide plane with a glide $^{c}/2$. These glide planes must come at intervals $^{b}/4$ and $\frac{3b}{4}$. We assume the molecule to have a centre of symmetry. This seems a reasonable assumption to make at this stage if we consider the chemical structure of the molecule, and other evidence of structures in some way related to the one under consideration. If we take this centre of symmetry at the origin 0, fig. 8, then any point (x,y,z,) and its inverse will, by the operation of the glide plane, give the following equivalent points

$$x,\ y,\ z, \qquad x, \tfrac{1}{2} - y,\ z + \tfrac{1}{2}$$

$$\bar{x},\ \bar{y},\ \bar{z}, \qquad \bar{x},\ y + \tfrac{1}{2},\ \tfrac{1}{2} - z \quad \text{or} \quad \bar{x},\ y - \tfrac{1}{2},\ -\tfrac{1}{2} - z.$$

The latter set of co-ordinates comes simply by subtracting one which brings us to a similar position in the next cell. The co-ordinates of the equivalent positions in the unit cell are then given by $\pm(x,\ y,\ z)$ and $\pm(x,\ \frac{1}{2} - y,\ z + \frac{1}{2})$. Now $F(hkl) = \sum e^{2\pi i(hx+ky+lz)}$ the summation extending over all the points in the unit cell. Substituting the values $\pm(x,\ y,\ z,);\pm(x,\ \frac{1}{2} - y,\ z + \frac{1}{2})$ in the above expression for F(hkl), the sin terms vanish and we have

$$F(HKL) = 2\cos 2\pi(hx + ky + lz) + 2\cos 2\pi(hx + {}^{k}/2 - ky + lz + {}^{l}/2)$$

$$= 4\cos 2\pi(hx + lz + \tfrac{k+l}{4})\cos 2\pi(ky - \tfrac{k+l}{4})$$

Considering spectra of the form 0K0 only

$$F(0K0) = 4\cos 2\pi({}^{k}/4)\cos 2\pi(ky - \tfrac{k}{4})$$

$$= 0 \text{ if K is odd.}$$

This is the condition governing a screw axis parallel to b, a condition not observed, although the intensities for 0K0, with K odd,

(were)

were found to be very small. If then we assume the molecule to have a centre of symmetry, it cannot be symmetrical about the origin chosen. The small intensity values for OKO, with K odd, suggested a small shift of the assumed symmetry centre of the molecule from the origin. From the glide plane condition such a shift can only be parallel to the y direction.

In fig.9 we assume a shift b along the y direction. Again, assuming the molecule to have a centre of symmetry, the equivalent points in the unit cell now have co-ordinates

$$\pm(x,\ y+b,\ z)\ ;\ \pm(x,\ \tfrac{1}{2}-y-b,\ z+\tfrac{1}{2}).$$

$$F(hkl) = e^{2\pi i(hx+ky+lz)}e^{2\pi i k b} + e^{-2\pi i(hx+ky+lz)}e^{2\pi i k b}$$

$$+ e^{2\pi i\left(hx-ky+lz+\frac{k+l}{2}\right)}e^{-2\pi i k b} + e^{-2\pi i\left(hx-ky+lz+\frac{k+l}{2}\right)}e^{-2\pi i k b}.$$

$$= 2e^{2\pi i k b}\cos 2\pi(hx+ky+lz) + 2e^{-2\pi i k b}\cos 2\pi\left(hx-ky+lz+\frac{k+l}{2}\right)$$

$$= 2\cos 2\pi kb\left[\cos 2\pi(hx+ky+lz) + \cos 2\pi\left(hx-ky+lz+\frac{k+l}{2}\right)\right]$$
$$+ i2\sin 2\pi kb\left[\cos 2\pi(hx+ky+lz) + \cos 2\pi\left(hx-ky+lz+\frac{k+l}{2}\right)\right]$$

$$= 4\cos 2\pi kb\cos 2\pi\left(hx+lz+\frac{k+l}{4}\right)\cos 2\pi\left(ky-\frac{k+l}{4}\right)$$
$$- i4\sin 2\pi kb\sin 2\pi\left(hx+lz+\frac{k+l}{4}\right)\sin 2\pi\left(ky-\frac{k+l}{4}\right)$$

We must now distinguish between two cases.

(k+l) even

$$F_{(hkl)} = 4 \cos 2\pi kb \cos 2\pi (hx+lz) \cos 2\pi ky$$
$$- i\, 4 \sin 2\pi kb \sin 2\pi (hx+lz) \sin 2\pi ky.$$

(k+l) odd

$$F_{(hkl)} = -4 \cos 2\pi kb \sin 2\pi (hx+lz) \sin 2\pi ky$$
$$+ i\, 4 \sin 2\pi kb \cos 2\pi (hx+lz) \cos 2\pi ky.$$

For this projection we are only interested in spectra of the type okl, and again we distinguish between two cases

okl with (k+l) even

$$F_{(okl)} = 4 \cos 2\pi\, kb \cos 2\pi lz \cos 2\pi ky$$
$$+ i\, 4 \sin 2\pi kb \sin 2\pi lz \sin 2\pi ky.$$

okl with (k+l) odd

$$F_{(okl)} = -4 \cos 2\pi kb \sin 2\pi lz \sin 2\pi ky$$
$$+ i\, 4 \sin 2\pi kb \cos 2\pi lz \cos 2\pi ky.$$

If we now put in f, the atomic scattering factor appropriate to the planes (okl), then the structure factors finally take the form.

(k+l) even

$$A(okl) = +4 \cos 2\pi kb \sum f \cos 2\pi lz \cos 2\pi ky$$
$$B(okl) = -4 \sin 2\pi kb \sum f \sin 2\pi lz \sin 2\pi ky.$$

(k+1) odd

$$A(okl) = -4 \cos 2\pi kb \sum f \sin 2\pi lz \sin 2\pi ky$$
$$B(okl) = 4 \sin 2\pi kb \sum f \cos 2\pi lz \cos 2\pi ky,$$

the summation being over all the atoms in the unit cell. The numerical value of the structure factor is given by

$$|F_{(okl)}| = \sqrt{A^2 + B^2} \quad , \text{ and } \quad \delta = \tan^{-1}(B/A)$$

Spectra of the form 00ℓ are present only with ℓ even and so we have

$$A(00\ell) = 4\sum f \cos 2\pi lz$$
$$B(00\ell) = 0$$

For spectra of the form 0K0 we again distinguish between two cases

$$\left.\begin{aligned} A &= 4 \cos 2\pi kb \sum f \cos 2\pi ky \\ B &= 0 \end{aligned}\right\} \text{ for K even}$$

$$\left.\begin{aligned} A &= 0 \\ B &= 4 \sin 2\pi kb \sum f \cos 2\pi ky \end{aligned}\right\} \text{ for K odd.}$$

These are all the structure factors necessary for the calculations of this projection.

FOURIER SYNTHESIS OF THE bc PROJECTION.

Preliminary Considerations.

A method of measuring the total energy reflected, known as the integrated reflection, was devised at an early date by W.H.Bragg. Following a detailed treatment by A.H.Compton (16), the following expression for the reflection from a small crystal of volume V, completely bathed in radiation of intensity I_o per square cm., can be derived

$$\int R(\theta) \frac{d\theta}{I_o} = \left(\frac{Ne^2}{mc^2}\right)^2 \left|F_{(hkl)}\right|^2 \lambda^3 \frac{1+\cos^2 2\theta}{2\sin 2\theta} V.$$

The integrated reflection $= \int R(\theta) \frac{d\theta}{I_o}$ where $R(\theta)$ is the radiation reflected at an angle θ, and the crystal rotates so that it has a chance of reflecting over the whole range of possible reflecting angles. The integrated reflection can also be written in the form $\frac{E\omega}{I_o}$, where E is the total energy reflected when the crystal rotates with constant angular velocity ω through the reflecting position. The above expression only applies to very small crystals where absorption effects can be neglected. Also, the expression applies only to "mosaic" crystals. The crystals under examination were very small and are assumed to be mosaic, so that the above expression can be applied directly without correction for absorption.

In the above expression if we substitute $\frac{E\omega}{I_o}$ for the integrated reflection and put $\frac{1+\cos^2 2\theta}{\sin 2\theta} = \phi$, then, since all the other terms entering the above expression are constants,

$$\frac{E\omega}{I_o} \propto |F(hkl)|^2 \phi$$

If we assume that the intensities I, measured for the various (okl) planes, are proportional to the integrated reflections, then we have

$$F(okl) \propto \sqrt{I/\phi}$$

All subsequent calculations of the structure factors from the experimentally determined intensities are based on the above assumption. It is obvious that all we can hope for is a relative set of F factors for the spectra recorded, related in some way to the integrated intensities of these spectra. The values I were already known for all the okl spectra, and it was necessary now to calculate the factor ϕ for all the spectra concerned.

Considering reciprocal axes, then for any reciprocal lattice we have

$$\underline{r}^* = h\underline{a}^* + k\underline{b}^* + l\underline{c}^*$$

$$|r^*|^2 = h^2\underline{a}^{*2} + k^2\underline{b}^{*2} + l^2\underline{c}^{*2} + 2hk\underline{a}^*\underline{b}^* + 2\,hl\underline{a}^*.\underline{c}^* + 2\,kl\underline{b}^*.\underline{c}^*$$

where $\underline{a}^*$, $\underline{b}^*$, and $\underline{c}^*$ are the primitive vectors of the reciprocal lattice net.

Also $d(hkl) = \frac{1}{(r^*)}$, and for a monoclinic lattice

$$\alpha = \gamma = 90$$

Substituting in the wellknown Bragg reflection formula $2d\sin\theta = n\lambda$, and considering the (okl) planes only,

$$\frac{\sin\theta}{\lambda} = \frac{\sqrt{k^2b^{*2} + l^2c^{*2}}}{2}$$

The above expression made it possible to calculate the value of $\frac{\sin\theta}{\lambda}$ for every (okl) plane. From tables compiled by R.W.James (and G.W.B.)

and G.W.Brindley (20) for the atomic scattering factors, fo, for light atoms and ions, graphs were plotted of $\frac{\sin\theta}{\lambda}$ against fo for oxygen, nitrogen and carbon atoms. From these graphs the values of f could be determined directly for any angle of scattering for all atoms giving rise to a diffracted beam. Using a set of valuesgiven in "Internationale Tabellen zur Bestimmung von Kristallstrukturen", volume 2, page 568, a graph of $\sin\theta$ against $\left\{ \frac{1+\cos^2 2\theta}{\sin 2\theta} \right\} = \phi$ was plotted. This gave the value of ϕ directly for any okl reflection.

The intensities I, and the values ϕ were now known for all the okl spectra round this zone. Substituting in the formula $F\,(okl) \propto \sqrt{I/\phi}$, the F factors for all such spectra were calculated, and the values so obtained were taken to represent the observed structure factors.

The lack of knowledge of the relative phase constants of these reflections makes it impossible to apply the Fourier Series method directly to the solution of this structure, unless other sources of information or assumptions about the structure are employed. The number and variety of atoms in the unit cell was determined by preliminary X-ray methods together with ~~the~~ chemical analysis. The atomic scattering factors of the atoms present were fairly accurately known, and the problem which remained to be solved was that of finding the positions of the various atoms in the unit cell which would account for the set of experimentally determined intensities. The positions of the atoms in the unit cell can be expressed by means of a geometrical structure

(factor)

factor, with three parameters for each atom. Various likely positions for the atoms, as indicated by the chemical structure, physical properties of the crystal (refractive indices, dimensions of the unit cell, size of the molecule etc.) and information from previous determinations of crystals in some ways resembling the one under investigation, can then be tested until agreement is obtained between the calculated and observed intensities. There is no general rule governing this process, which may be called analysis by trial. When a good measure of agreement is obtained and the main outlines of the structure are clear, the calculated phase constants can be combined with the experimentally determined amplitudes, and a Fourier synthesis carried out. The results will generally lead to more precise values for the atomic co-ordinates. From these revised parameters the phase constants can be recalculated, bringing in some weaker reflections, previously omitted, and the process completed with a more complete Fourier series. In this way, by a method of successive approximation, the true structure can be obtained.

Testing the assumed Structure for the ool and oko Spectra .

To start with it was assumed that the molecule itself had a centre of symmetry, and that the two benzene rings were in the same plane. From packing considerations, described earlier in this work, it appeared that the most likely way of packing the molecules to give a reasonably good fit, was with the long axis of the molecule making an angle of approximately 35 degrees with the b axis, and the NO_2 group twisted about this long axis until the plane containing the oxygen atoms made an angle of about 25degrees

(with)

with the plane of the benzene rings. It was also assumed that all the C and N atoms in the molecule lay in the (I00) plane, so that the x co-ordinates of such atoms were zero. This was the structure assumed as a first approximation, and with the atoms in these positions the y and z parameters for the 9 atoms concerned were calculated. The parameters were expressed in angular co-ordinates and as fractions of the unit cell edges. With these parameters it was now possible to calculate the F factors, and to compare these with the observed values of F(okl). This was a tedious and long process owing to the complexity of the structure factor formulae for the (okl) planes, and the large number of atoms in the unit cell. To save time and labour it was advisable first to get good agreement between the calculated and observed values of F(hkl) for the more simple spectra, and then to extend the calculations to the more general (okl) planes.

Following this line of reasoning, attention was turned to the ool spectra, where the structure factor for such planes is given by the comparatively simple expression

$$F(ool) \quad 4 \sum f \cos 2\pi lz.$$ (see page 57.)

The b shift of the molecule from the origin does not enter into the above expression. From packing considerations it was obvious that, to allow for the necessary space, this b shift parallel to the y direction had to be very small. The small intensity values of the oko spectra, with k odd, seemed to confirm this deduction, for with no shift such oko spectra would have been absent. As a first approximation then we can take the centre of symmetry of the

(molecule)

molecule at the origin, for, since we are only dealing with the ool spectra, the z parameters will not be affected by such an assumption.

As we were trying to establish an agreement between only a few spectra to start with, it was necessary to know the relative intensities of these ool spectra as accurately as possible.In previous determinations these spectra came on different films, and during the process of standardisation serious errors might have set in. Also because of the big c spacing (c = 15.39 A) it was often difficult to distinguish between spectra such as 060 and 061, so that in such cases an element of doubt was always present unless removed by setting the crystal so as to bring in only one of these spectra. For accurate work it was necessary then to get all the ool spectra on the same film, with the same conditions of developing and exposure. A complete rotation of the crystal was out of the question, for, on account of the large number of spectra round this zone, considerable overlapping and confusion was anticipated, and other methods had to be tried.

The a axis of this crystal was very small (a = 3.77 A), and measurements on the a* c* net indicated that, for a crystal rotating about the b axis and given a suitable 50 degrees oscillation, all the necessary ool spectra would be recorded on the same film without any possibilities of interference or overlapping.A 50 degree cam was carefully constructed and tested for uniform speed of oscillation until, within the errors of observation , the speed was uniform to within 2%. A suitable crystal was cut and mounted

(about)

about the b axis. The outline of the crystal used was very nearly cubic, with the cube edge just under 0.2 mms. In this way the mean path of the X-rays through this crystal was approximately the same as for the crystal used in the previous observations. With the adjustments carefully made, three different exposures were taken. The data from the corresponding photometer curves are given below. One such photometer trace, showing the ool peaks, is shown in fig 10.

(tables)

Index	ho cms.	h cms.	ho sec.	h sec.	(h-ho) sec.	
002	4.50	0.80	17.2	90.5	73.3	Film 1
004	5.33	2.69	12.0	35.7	23.7	
006	5.23	0.92	12.8	83.5	70.7	
008	5.20	0.59	13.0	107.0	94.0	
0010	5.88	5.02	8.0	14.0	6.0	
0012	-	-	-	-	-	
0014	6.17	5.81	6.2	8.7	2.5	
002	4.14	0.87	20.0	86.0	66.0	Film 2
004	5.13	2.79	13.3	34.3	21.0	
006~~5.30~~	5.30	0.90	12.2	84.5	72.3	
008	5.22	0.51	12.9	115.0	102.1	
0010	5.85	5.10	8.4	13.5	5.1	
0012	-	-	-	-	-	
0014	6.20	5.80	6.1	8.9	2.8	
002	5.22	1.95	12.8	49.0	36.2	Film 3
004	5.71	3.96	9.5	21.6	12.1	
006	5.88	1.96	8.1	49.0	40.9	
008	5.81	1.45	8.8	61.7	52.9	
0010	6.10	5.72	7.0	9.2	2.2	
0012	-	-	-	-	-	
0014	-	-	-	-	-	

The measured intensities for films 1 and 2 are very nearly the same,

(WITH)

with film 3 about half these values. The mean intensity of these spectra was taken as $I = \frac{1+2+2\times3}{3}$. To express these values on the same scale as the intensities previously determined, it was found necessary to multiply by a factor 4.0, giving the final values of $I_{(oo\ell)}$, expressed to the nearest whole number, as

Index	I (sec.)
002	282
004	92
006	300
008	404
0010	20
0012	-
0014	12

Numerous calculations were made, varying the twist on the NO_2 groups, and the angle that the long axis of the molecule made with the b direction, to try to establish agreement between observed and calculated values of F (ool). It was at this stage of the analysis that the great help that would have been afforded by absolute intensity measurements were fully realised. The observed values of F (okl) did not give more than a relative estimate of the rising and falling off of the intensities, and the observed and calculated F factors could not be compared directly, as is the case when absolute intensity measurements are made. It was therefore impossible to say when the observed and calculated values of F agreed for any one spectrum, All that could be hoped

(for)

for was the same general way of rising and falling off in the intensity for F (ool) observed and calculated. The limitations introduced by adopting these methods of measuring intensities cannot be stressed sufficiently, when we compare them with the powerful methods afforded by absolute intensity determinations.

After many trials it was finally found that an angle of 30 degrees with the b axis, and a twist of 30 degrees for the NO_2 group gave the best agreement between observed and calculated values of F (ool). With this agreement it was found that the scale chosen for expressing the observed intensities was such that the values of F observed and calculated could be compared directly if the factor 4 in the expression $F(ool) = 4\sum f \cos 2\pi lz$ was left out. This was done in all subsequent calculations, remembering to multiply the observed values of F (okl) by this factor 4 when it finally came to evaluating the Fourier series. The numerical agreement between F (ool) observed and calculated finally obtained is given in the following table. For comparison purposes the factor 4 has been omitted in the calculated values of F (ool).

(table)

hkl	$\sqrt{\frac{I}{\phi}} = F$	F calc.
002	$\sqrt{\frac{282}{9.85}} = 5.3$	2.5
004	$\sqrt{92}/4.7 = 4.4$	3.5
006	$\sqrt{\frac{300}{2.9}} = 10.1$	8.4
008	$\sqrt{\frac{404}{2.0}} = 14.2$	12.2
0010	$\sqrt{\frac{20}{1.4}} = 3.8$	4.3
0012	- -	0.41
0014	$\sqrt{12}/1.0 = 3.5$	4.0
0016	$\sqrt{10}/1.1 = 3.0$	3.7

The next step was to see how the structure factors calculated from these final y and z parameters compared with the observed values for the oko spectra, and secondly to determine this b shift of the molecule which, for the first approximation, had been taken as zero, as this in no way affected the z parameters for calculating F (ool). It was necessary again to have all the oko spectra recorded on the same film. This was done in a way similar to that previously described for the ool spectra. The same crystal specimen was used, mounted about the c axis, involving the use of the a* b* reciprocal lattice net. Again all the possibilities of overlapping spectra or ambiguity were eliminated by using the 50 degree cam. The structure factors used are given by the expression

$$F\,(oko) = \cos 2\pi kb \sum f \cos 2\pi ky \qquad \text{for k even}$$

$$F\,(oko) = \sin 2\pi kb \sum f \cos 2\pi ky \qquad \text{for k odd,}$$

(again)

again leaving out the factor 4.

For every oko spectrum the expression under the summation sign was evaluated, giving the structure factor in the form

$$F\ (\text{oko}) = \begin{matrix}\cos 2\pi kb, \text{or} \\ \sin 2\pi kb\end{matrix} \left\{ \text{a numerical value depending on k.} \right\}$$

These values were then directly compared with the observed values of F (oko), and a mean value calculated for $(2\pi b)$ to give the best possible agreement between F (oko) observed and calculated. The mean value for $2\pi b$ was found to be 7 degrees, and substituting this in the structure factor expressions, the following values for F (oko) observed and calculated were obtained.

hkl	$\sqrt{I}/\phi$ = F (obs.)	F (calc.)
010	$\sqrt{54}/12.3$ = 2.1	1.4
020	$\sqrt{\frac{331}{5.8}}$ = 7.5	9.4
030	$\sqrt{18}/3.8$ = 2.2	2.8
040	$\sqrt{\frac{5.4}{2.7}}$ = 1.4	2.1
050	$\sqrt{\frac{6.6}{1.96}}$ = 1.8	1.7
060	$\sqrt{15}/1.5$ = 3.2	.43 ?
070	- = -	1.3
080	$\sqrt{\frac{121}{1.05}}$ = 10.7	8.9

Calculation of F (okl) from the assumed Structure.

Several further attempts were made to improve upon this agreement, by altering the angle that the long axis of the molecule made with the b axis, and by altering the twist on the NO_2 group, but all efforts failed. To get better agreement it appeared that something else had to be done to the molecule, such as a small tilt of the benzene rings, or a dishing of the Oxygen atoms in the NO_2 group, as was found by R.W.James, G.King, and H.Horrocks (8) when examining the crystal structure of para-dinitrobenzene. The molecule had so many degrees of freedom that it was not considered advisable to attempt any other adjustments of the parameters at this stage. It was decided to calculate the F factors for the more general (okl) planes, and if there existed a reasonable agreement between the observed and calculated values, to evaluate the Fourier series, and determine any change of parameters from this projection.

Before any further calculations were made, the validity of this assumed structure was tested in a different way. If we inspect the measured intensities, given on page 53b., we find that spectra 043, 008, and 0411 have the highest F values. The atoms must then be so distributed that they lie approximately in sheets on these (043), (008), and (0411) crystal planes. Traces of these planes were drawn on the bc face of the unit cell. It was at once obvious that with the molecules in the assumed positions, the various atoms in the unit cell were roughly distributed along these parallel sheets, and would give rise to strong calculated F factors. This then seemed to verify that the

(assumed)

assumed positions of the atoms would give results consistent with those observed. Here again the advantages of absolute measurements were realised. We may find, for instance, that the 0411 reflection is so strong that its value of F (0411) is very nearly the maximum which could be given if all the atoms of the crystal were contributing waves of the same phase along this direction, showing at once that the atoms are so arranged that they lie in sheets on the crystal planes(0411). The intensity measurements made were expressed entirely on an arbitrary scale, so that no such simple relationship existed between F (obs.) and F (max.) for any one reflection. It was impossible to say what percentage of the possible maximum was observed, and so get some hint as to the approximate distribution of the atoms on these sheets. In the case under consideration a "strong" reflection did not mean anything in the real sense of the word, and might quite easily be 40% or less of the possible maximum. All we could say was that a certain spectrum was strong compared to others, and hence the atomic arrangement for such a strong reflection must conform much more to distribution in parallel sheets than will be the case for the weaker reflections.

So far the assumed structure gave results that were consistent with those observed, and there was reason to believe that it could not be very far from the truth. The more general F (okl) factors were now calculated. The general agreement between F (obs.) and F (calc.) was reasonable, taking all the experimental difficulties into account, particularly the way of measuring and standardising the intensities. Again leaving out the factor 4 coming in front of

(the summation sign)

the summation sign for $F(o\kappa\ell)$ calculated, the following table gives the results obtained for F (okl) observed and calculated.

hkl	$\frac{\sin\theta}{\lambda}$	F (obs.)	F (calc.)
002	.065	5.3	2.5
004	.130	4.4	3.5
006	.195	10.1	8.4
008	.260	14.2	12.2
0010	.325	3.8	4.3
0012	.390	-	0.41
0014	.455	3.5	4.0
0016	.520	3.0	3.7
010	.052	2.1	1.4
020	.105	7.5	9.4
030	.157	2.2	2.8
040	.209	1.4	2.1
050	.262	1.8	1.7
060	.314	3.2	0.43
070	.366	-	1.3
080	.418	10.7	8.9
011	.062	1.8	1.9
012	.083	12.8	10.5
013	.111	11.9	13.9
014	.140	3.9	2.3
015	.171	1.5	1.3
016	.202	1.5	0.93
017	.233	2.0	1.2

(cont.)

(continued)

hkl	$\frac{\sin\theta}{\lambda}$	F (obs.)	F (calc.)
018	.265	3.8	0.98
019	.297	1.8	0.26
0110	.329	3.3	1.4
0111.	.361	3.9	4.9
0112	.393	-	1.4
021	.110	6.2	6.9
022	.123	8.7	9.9
023	.143	8.4	4.9
024	.167	6.8	2.3
025	.193	8.0	6.7
026	.221	3.2	2.5
027	.250	2.2	0.79
028	.280	3.5	3.6
029	.311	2.3	0.41
0210	.341	1.9	3.6
0211	.372	2.0	1.2
0212	.404	-	0.41
031	.160	1.8	1.8
032	.170	4.5	3.3
033	.185	7.9	7.7
034	.204	2.7	0.69
035	.226	4.3	5.2
036	.251	6.9	5.9
037	.276	4.9	1.8

(cont.)

(continued)

hkl	$\frac{\sin\theta}{\lambda}$	F (obs.)	F (calc.)
038	.304	2.1	1.1
039	.333	2.7	3.5
0310	.361	2.0	3.0
0311	.390	3.6	2.2
0312	.412	2.6	3.3
0313	.451	5.0	6.8
041	.212	3.2	1.1
042	.219	5.8	4.5
043	.231	14.6	12.3
044	.246	7.8	5.0
045	.265	6.0	1.03
046	.281	1.7	1.9
047	.309	1.6	0.65
048	.334	2.3	1.7
049	.260	4.8	5.9
0410	.387	3.5	5.5
0411	.414	10.8	12.4
0412	.443	3.3	4.6
051	.264	3.0	3.0
052	.269	1.8	0.55
053	.279	3.0	2.9
054	.292	3.8	1.4
055	.308	7.1	3.2
056	.326	3.8	4.8

(cont.)

(continued)

hkl	$\frac{\sin\theta}{\lambda}$	F (obs.)	F (calc.)
057	.347	1.4	1.0
058	.369	1.6	1.8
059	.392	3.0	3.3
0510	.417	2.4	1.5
0511	.443	2.2	0.87
0512	.470	2.7	1.7
0513	.497	4.6	4.1
061	.316	2.8	2.1
062	.321	3.4	1.2
063	.329	1.5	3.6
064	.340	2.7	1.5
065	.353	2.0	4.5

The calculated values of F (okl) are given as numerical values only, the signs being left out for the present.

Summation Equations for the bc Projection.

It was necessary now to make the actual Fourier summation. The method used was that given in a paper by H.Lipson and C.A.Beevers (21), but the summation equations given by them were modified to fit the particular case in hand.

(the summation)

The summation to be made is

$$\mathcal{S}(yz) = \sum_{-K}^{+K} \sum_{-L}^{L} F(okl) \exp i\,(ky+lz) \quad \ldots\ldots\ldots (A)$$

Here K and L are the maximum values of the k and l indices for the planes to be used. This can be written

$$\mathcal{S}(yz) = \sum_{-K}^{+K} \sum^{+L} \left\{ F(okl) \exp i\,(ky+lz) + F(o\bar{k}\bar{l}) \exp -i\,(ky+lz) \right\} + \sum_{1}^{K} \left\{ F(oko) \exp i\,(ky) + F(o\bar{k}o) \exp -i\,(ky) \right\} + F(ooo) \ldots (B)$$

Since F(okl) and F(o$\bar{k}\bar{l}$) are conjugate, we can put

$$F(okl) = \left|F(okl)\right| e^{i\delta(kl)}$$

and $F(o\bar{k}\bar{l}) = \left|F(okl)\right| e^{-i\delta(kl)}$, and hence

$$\mathcal{S}(yz) = 2\sum_{-K}^{+K} \sum_{1}^{+L} \left\{ \left|F(okl)\right| \cos\left(ky+lz+\delta_{(kl)}\right) \right\} + 2\sum_{1}^{K} \left\{ \left|F(oko)\right| \cos\left(ky+\delta_{(ko)}\right) \right\} + F(ooo) \quad \ldots (C)$$

Put $\left|F(okl)\right| \cos\delta_{(kl)} = C_{(kl)}$, $\left|F(okl)\right| \sin\delta_{(kl)} = S_{(kl)}$

Equation (C) can be expanded in the form

(equation)

$$\rho(yz) = 2\sum_{-K}^{+K}\sum_{l}^{+L} \left|F(okl)\right| \left\{ \cos(ky+lz)\cos\delta_{(kl)} - \sin(ky+lz)\sin\delta_{(kl)} \right\}$$

$$+ 2\sum_{l}^{K} \left|F(oko)\right| \left\{ \cos ky \cos\delta_{(ko)} - \sin ky \sin\delta_{(ko)} \right\} + F(ooo)$$

$$= 2\sum_{-K}^{K}\sum_{l}^{L} \Big[C_{(kl)} \left\{ \cos ky \cos lz - \sin ky \sin lz \right\}$$

$$- S_{(kl)} \left\{ \sin ky \cos lz + \cos ky \sin lz \right\} \Big]$$

$$+ 2\sum_{l}^{K} \left\{ C_{(ko)} \cos ky - S_{(ko)} \sin ky \right\} + F(ooo)$$

or

$$\rho(yz) = 2\sum_{l}^{K}\sum_{l}^{L} \Big[\; C_{(kl)} \left\{ \cos ky \cos lz - \sin ky \sin lz \right\}$$

$$- S_{(kl)} \left\{ \sin ky \cos lz + \cos ky \sin lz \right\}$$

$$+ C_{(\bar{k}l)} \left\{ \cos ky \cos lz + \sin ky \sin lz \right\}$$

$$- S_{(\bar{k}l)} \left\{ -\sin ky \cos lz + \cos ky \sin lz \right\} \Big]$$

$$+ 2\sum_{l}^{L} \left\{ C_{(ol)} \cos lz - S_{(ol)} \sin lz \right\}$$

$$+ 2\sum_{l}^{K} \left\{ C_{(ko)} \cos ky - S_{(ko)} \sin ky \right\} + F(ooo). \qquad \text{(D)}$$

(extra term on account of $\sum_{l}^{K}$ which leaves out K = 0 term.)

$$\rho(yz) = 2\sum_{l}^{K}\sum_{l}^{L} \Big[\left\{ C_{(kl)} + C_{(\bar{k}l)} \right\} \cos ky \cos lz$$

$$- \left\{ C_{(kl)} - C_{(\bar{k}l)} \right\} \sin ky \sin lz$$

$$- \left\{ S_{(kl)} - S_{(\bar{k}l)} \right\} \sin ky \cos lz$$

$$- \left\{ S_{(kl)} + S_{(\bar{k}l)} \right\} \cos ky \sin lz. \Big]$$

$$+ 2\sum_{l}^{L} \left\{ C_{(ol)} \cos lz - S_{(ol)} \sin lz \right\}$$

$$+ 2\sum_{l}^{K} \left\{ C_{(ko)} \cos ky - S_{(ko)} \sin ky \right\} + F(ooo) \qquad \text{- - - - (E)}$$

Put $A(oz) = 2\sum_{1}^{L}\{C_{(ol)}\cos lz - S_{(ol)}\sin lz\} + F(ooo)$

$A(kz) = 2\sum_{1}^{L}\{(C_{(kl)}+C_{(\bar{k}l)})\cos lz - (S_{(kl)}+S_{(\bar{k}l)})\sin lz\}+2C_{(ko)}$

$B(kz) = 2\sum_{1}^{L}\{(C_{(kl)}-C_{(\bar{k}l)})\sin lz+(S_{(kl)}-S_{(\bar{k}l)})\cos lz\}+2S_{(ko)}.$

These then are the preliminary summations to be made, the final summations being given by

$$\int(yz) = A(oz)+\sum_{1}^{K} A(kz)\cos ky - \sum_{1}^{K} B(kz)\sin ky.$$

This represents the Fourier summation in its most general form. We now apply these equations to the actual case under consideration. Referring to the structure factor equations (page 56,57), there are two cases to consider, 1). when (k+1) is even, and 2). when (k+1) is odd.

<u>0$\bar{k}$l</u> <u>1). when (k+1) is even.</u>

The A term does not change sign, but remains the same as for okl with (k+1) even.

The B term changes sign twice, in sin 2πkb and sin 2πky, and so the sign remains the same. Both A and B have the same sign for o$\bar{k}$l as for okl, and therefore

$\tan^{-1} B/A$ is the same.

<u>2)(k+1) odd.</u>

The A term changes sign once in sin 2πky

The B term changes sign once in sin 2πkl.

Both A and B change sign, but $\tan^{-1} B/A$ is still the same.

(following)

Following a similar line of reasoning we find

okĪ 1) (k+1) even, $\tan^{-1} B/A$, okĪ has an opposite sign to okl,

2) (k+1) odd, $\tan^{-1} B/A$, okĪ has an opposite sign to okl.

oklĪ 1) (k+1) even, $\tan^{-1} B/A$, $o\bar{k}\bar{e}$ has an opposite sign to okl,

2) (k+1) odd, $\tan^{-1} B/A$, $o\bar{k}\bar{e}$ has an opposite sign to okl.

Now $|F(okl)| = \sqrt{A^2 + B^2}$, and $\delta = \tan^{-1} B/A$

Hence $|F(okl)| = |F(o\bar{k}l)| = |F(o\bar{k}\bar{I})| = |F(ok\bar{I})|$

$\delta(okl) = \delta(o\bar{k}l) = -\delta(o\bar{k}\bar{I}) = -\delta(ok\bar{I})$

If we turn back now to our preliminary summation expressions, B, (page 77), we see that only spectra okl and o$\bar{k}$l occur. We have two cases to consider

1) (k+1) even, then $C(okl) = C(o\bar{k}l)$, and $S(okl) = S(o\bar{k}l)$

2) (k+1) odd, then $C(okl) = -C(o\bar{k}l)$, and $S(okl) = -S(o\bar{k}l)$

Substituting these in the preliminary equations A(oz), A(kz) and B(kz) (page 78) we have

For (k+1) even

$$A(oz) = 2\sum_{l}^{L}\{C(ol)\cos lz - S(ol)\sin lz\} + F(ooo)$$

$$A(kz) = 2\sum_{l}^{L}\{2\,C(kl)\cos lz - 2\,S(kl)\sin lz\} + 2\,C(ko)$$

$$B(kz) = 2\,S(ko).$$

For (k+1) odd.

$$A(oz) = 2\sum_{l}^{L}\{C(ol)\cos lz - S(ol)\sin lz\} + F(ooo)$$

$$A(kz) = 2\,C(ko)$$

$$B(kz) = 2\sum_{l}^{L}\{2\,C(kl)\sin lz + 2\,S(kl)\cos lz\} + 2\,S(ko)$$

(the expressions)

The expressions for A(oz), A(kz), B(kz) can be further simplified.

(k+1) even.

A(oz) involves spectra of the form ool only. These occur only for l even; hence S(ol) is zero. The term 2 S(ko) can in this case be present only for even values of k, hence S(ko) is zero.

Finally then

$$A(oz) = 2 \sum_{l}^{L} \{ C(ol) \cos lz \} + F\,ooo$$

$$A(kz) = 2 \sum_{l}^{L} \{ 2\,C(kl) \cos lz - 2\,S(kl) \sin lz \} + 2\,C(ko)$$

$$B\,kz = 0$$

(k+1) odd.

Spectra of the form ool are absent for l odd, and C(ko) is zero for odd values of k. Hence

$$A(oz) = 0$$

$$A(kz) = 0$$

$$B(kz) = 2 \sum_{l}^{L} \{ 2\,C(kl) \sin lz + 2\,S(kl) \cos lz \} + 2\,S(ko)$$

To simplify, and not to make the coefficients in the Fourier series unnecessarily large, we divide throughput by a factor 4, and finally arrive at the following preliminary summations.

$A_1(kz) = \sum_{l}^{L} \{ C(kl) \cos lz - S(kl) \sin lz \}$ for (k+1) even

$B_1(kz) = \sum_{l}^{L} \{ C(kl) \sin lz + S(kl) \cos lz$ for (k+1) odd.

$A_2 kz = \frac{1}{2}\,C(ko)$ for k even

$B_2(kz) = \frac{1}{2}\,S(ko)$ for k odd.

$\frac{1}{4}\,A(oz) = \sum_{l}^{L} \{ \frac{1}{2}\,C(ol) \cos lz \} + \frac{1}{4}\,F(ooo)$, thus making

$$A(kz) = 4 \left[A_1(kz) + A_2(kz) \right]$$

$$B(kz) = 4 \left[B_1(kz) + B_2(kz) \right]$$

Evaluating the two- dimensional Fourier Series.

Before these summations could be made the values of C(kl) and S(kl) had to be known. For this it was necessary to calculate the phase angles of all the okl spectra recorded. These values of δ(okl) were calculated from the formula, $\delta_{(okl)} = \tan^{-1} B/A$, using the calculated values of A and B. Great care was taken with regard to the signs of A and B for determining in which quadrant δ(okl) was. Using these calculated values of δ, $\cos\delta$ and $\sin\delta$ were determined, and then combined with the experimentally determined values of F(okl). Here the observed values of F(okl) were multiplied by a factor 4, to make the scale expressing these values the same as for the true calculated F(okl) values, where the factor 4 outside the summation sign has been omitted so far for the purposes of comparing observed and calculated F factors directly. This will be clear if we refer to page 67 where this point is discussed. These F(okl) observed values were then expressed to the nearest whole number. The following tables give the final results obtained, keeping values of (k+1) odd and even separate.

(k+1) odd.

Index	F obs.	δ °	F $\cos\delta$	F $\sin\delta$
010	8	270	0	-8
030	9	270	0	-9
050	7	270	0	-7
070	-	270	0	0
012	51	171	-50	8
014	16	357	16	3

(cont.)

Index	F obs.	δ°	F cos δ	F sin δ
016	6	2	6	0
018	15	205	-14	-6
0110	13	149	-7	7
0112	-		0	0
021	25	30	22	13
023	34	209	-30	-16
025	32	350	32	-6
027	9	1	9	0
029	9	115	-4	8
0211	8	299	4	-7
032	18	103	-4	18
034	11	189	-11	-2
036	28	194	-27	-7
038	8	360	8	0
0310	8	135	-6	6
0312	10	212	-9	-5
041	13	28	11	6
043	58	188	-57	-8
045	24	119	-12	21
047	6	10	6	1
049	19	183	-19	-1
0411	43	183	-43	-2
052	7	263	-1	-7
054	15	356	15	-1
056	15	158	-15	6
058	6	309	4	-5

(cont.)

Index	F obs.	$\delta°$	F cos δ	F sin δ
0510	10	266	-1	-10
0512	11	109	-4	10
061	11	35	9	6
063	6	164	-6	2
065	8	15	8	2

(k+l) even.

Index	F obs.	$\delta°$	F cos δ	F sin δ
002	22	0	22	0
004	18	180	-18	0
006	40	0	40	0
008	57	0	57	0
0010	15	180	-15	0
0012	-		0	0
0014	14	180	-14	0
0016	12	180	-12	0
020	34	0	34	0
040	6	0	6	0
060	13	0	13	0
080	38	180	-38	0
011	7	223	-5	-5
013	48	357	48	-3
015	6	170	-6	1
017	8	178	-8	0
019	7	304	4	-6

(CONT.)

Index	F obs.	$\delta°$	F cos δ	F sin δ
0111	16	359	16	-0.3
022	35	184	-35	-3
024	27	175	-27	2
026	13	146	-12	7
028	14	354	14	-2
0210	8	177	-8	1
0212	-		0	0
031	7	236	-4	-6
033	32	9	32	5
035	17	208	-15	~~9~~8
037	20	189	-20	-3
039	11	354	11	-1
0311	14	343	13	-4
0313	20	196	-19	-6
042	23	220	-18	-15
044	31	283	7	-30
046	7	75	2	7
048	9	291	3	-8
0410	14	248	-5	-13
0412	13	289	4	-12
051	12	236	-7	-10
053	12	102	-3	12
055	28	297	13	-25
057	6	340	6	-2
059	12	181	-12	-2

(cont.)

Index	F obs	$\delta°$	F cos δ	F sin δ
0511	9	54	5	7
0513	18	317	13	-12
062	14	313	10	-10
064	11	332	10	-5

For convenience two separate tables were made out for C(kl) and S(kl), keeping (k+l) odd and even separate, which could be applied directly to the final preliminary summation expressions. This meant of course putting in the values $\frac{1}{2}$ C(ko), $\frac{1}{2}$ S(ko), $\frac{1}{2}$ C(ol), $\frac{1}{4}$ F(ooo) directly with the values C(kl) and S(kl) given in the previous two tables. The value F(ooo) represents the total number of electrons in the unit cells, which for this crystal comes to 252, hence the value $\frac{1}{4}$ F(ooo) used for compiling these two tables was 63.

For evaluating these preliminary summations a set of strips, prepared by M.Lipson and C.A.Beevers, was used. The cosine strips had index values 0 to 20, and the sine strips 1 to 20 inclusive. For each index there were strips of amplitudes $\overline{99}$ to 99. The functions were plotted at intervals of 6 degrees, so that a strip corresponding to A sin hx, had printed on it the value of A sin $\frac{2\pi nh}{60}$, where n has values from 0 to 15. This division of the cell-edge into 60 parts was found to be directly suitable if the maximum index was between 11 and 20, as was the case for the l index. The maximum k index was only 8, and so it was advisable to make the interval of division of this edge $\frac{1}{30}$. This was done most simply by considering a synthesis of two unit cells to be performed, the short edge being

(considered)

considered as doubled, and one of the indices of each plane, referred to this doubled cell, was doubled. Thus all that was necessary to obtain an interval $\frac{1}{30}$ in the b direction, was to double the k indices of the F(okl)'s, and then proceed in the usual way. The strips then gave the projection over the range y = 0 to 0.50 directly, instead of from y = 0 to 0.25. During these preliminary summations, the values of l even and l odd were kept separate, for the purposes of extending the summations. This extension can best be described by quoting an example. Suppose we wish to sum the expression $A_1(kz)$ for 2k = 2.

$$A_1(kz) = \sum_{l}^{L} \left\{ C(kl) \cos lz - S(kl) \sin lz \right\} \qquad \text{for } (k+l) \text{ even.}$$

Here k = 1 and therefore l is odd.

The numbers printed on the corresponding strips give the values of C(kl) cos lz and S(kl) sin lz directly from z = 0 to 0.25, or for the interval z = o to $\pi/2$. Making the necessary additions of the numbers given on the strips to be used here, then for this interval the summation is simply given by (C + S), where $C = \sum_{l}^{L} C(kl) \cos lz$, and $S = \sum_{l}^{L} S(kl) \sin lz$.

For l odd, cos lz is antisymmetrical about $\pi/2$, so that the summation for the interval z = 0.25 to 0.50 is given directly by -(C + S).

Similarly if we are summing $A_1(kz)$ for 2k = 4, i.e. k even and therefore l even, the summations for the intervals z = 0 to 0.25 and z = 0.25 to 0.50, are given directly by (C - S) and (C + S) respectively.

In this way the preliminary summations were completed and extended to half the cell edge in the z direction. The various

(terms)

terms were collected and arranged, ready to be used in the final summation, given by the expression

$$\int(yz) = A(oz) + \sum_{1}^{K} A(kz) \cos ky - \sum_{1}^{K} B(kz) \sin ky.$$

The k index had been doubled, hence for this summation only even values of k occurred. This doubling of k implied that the values printed on the strips gave the summation directly for the interval y = 0 to 0.50, and it could easily be extended to give the range y = 0 to 1.00. This gave the projection on the bc plane for half the unit cell, and using the glide plane condition the projection was extended to cover the whole unit cell.

The plane bc was drawn accurately to scale (4 cms. representing 1 A) on a sheet of drawing paper. The b and c axes were divided into 30 and 60 equal parts respectively, and through these points of division lines were drawn parallel to the b and c directions. At each of these points of intersection a value of $\int(yz)$, as determined from the Fourier synthesis, was written, and by the usual method contour lines were drawn at levels 100, 150, 200, 250, 300, and 350 where possible.

The maxima in the projection were very clear and could be interpreted without any difficulty. To express these contours in terms of electrons per A^2 we proceed as follows. The actual final summation made in this case was

$$\int(yz) = \tfrac{1}{4} A(oz) + \tfrac{1}{4}\sum_{1}^{K} A(kz) \cos ky - \tfrac{1}{4}\sum_{1}^{K} B(kz) \sin ky.$$

The reasons for dividing through by this factor 4 are given under the calculations of these summations, (see page 80). Hence a contour at 100 on this projection really means one at 400 if expressed on the proper)

the proper scale. We now have to divide this by the area of the plane on which the unit cell was projected. The area of the bc plane is equal to $(15.39 \times 9.56)A^2$, so that the first contour line on this projection represents $\frac{400}{15.39 \times 9.56} = 2.72$ electrons per A^2. On this projection then the contours are at intervals of 1.36 electrons per A^2, the outer line being the 2.72 electron contour. The contour diagram drawn from the values of $\rho(yz)$ for the projection on the bc face, viewed parallel to a, is shown in fig. 11. This contour diagram may be interpreted with the help of the key diagram, fig. 12. which shows the structure projected on the bc plane.

Deduction from the bc Projection.

When it came to determining the y and z parameters from the bc projection there was some doubt as to the validity of this projection. It was found that the y and z parameters determined from the maxima of the contour diagrams in fig. 11. agreed very closely with the parameters assumed for the probable structure. The agreement between assumed and determined parameters, expressed in A units and considering only one half of the molecule, is indicated in table A, with a discussion on this agreement immediately following.

(table A)

TABLE A.

Atom	y(assumed) A	y(determined) A	z(assumed) A	z(determined) A
C_1	0.641	0.34 ?	0.370	0.38
C_2	0.641	0.57	1.760	1.73
C_3	1.844	1.75	2.455	2.46
C_4	3.048	2.90	1.760	1.79
C_5	3.047	2.92	0.370	0.47
C_6	1.844	1.68	-0.325	-0.28
N_7	4.373	4.18	2.525	2.54
O_8	4.377	4.15	3.598	3.60
O_9	5.304	4.93	2.092	2.05

It is evident from the above table that the assumed and determined z parameters are in good agreement. The differences in the y parameters are explained as follows. Structure factor calculations showed that there must be a shift of the molecule in the b direction from the origin chosen. It was evident from packing considerations that, to allow for the necessary space, such a shift could only be very small, and as a first approximation the assumed symmetry centre of the molecule was taken at the origin, and the y and z parameters of the various atoms were calculated for the molecule in this position. The bc projection, fig. 12, showed the shift of the molecule from the origin clearly, and on this projection the y and z parameters were measured from the origin 0. The mean value of the b shift of the molecule from the origin calculated from this projection came to 0.16 A. If now this

(calculated)

calculated b shift is subtracted from each of the assumed y parameters given in table A, we again get good agreement between the assumed and determined values of y for the nine atoms under consideration.

It is evident from this agreement between the parameters that if a second projection were made using these redcterminod parameters, the general outline of the structure would not change appreciably and the actual positions of the atoms, given as maxima on the contour diagram in fig. 11., would hardly change at all. The determination of parameters from the projection could not be pushed too far, always taking the unavoidable experimental errors, and particularly the way of measuring intensities, into account, and considering the way the determined parameters varied when, for example, the sides of the benzene ring were measured, the benzene ring being known to approximate very closely to a regular hexagon.

The bc projection gave a good outline of the molecules, and showed clearly how they packed. It suggested that the two benzene rings in the molecule were co-planar, and that there may be some tilt of the plane of the rings relative to the bc plane, but that such a tilt is not very large. It further suggested that the line joining the two Oxygen atoms in the nitro group was inclined to the plane bc, and it has already beenpointed out that, to pack the molecules into the available space, the NO_2 group had to be twisted about the long axis of the molecule.

A more detailed account of the measurements obtained from the bc projection will be given under the description of the molecule.

(It must)

It must be pointed out that we are only dealing with projected distances, and the finer details of the structure cannot be determined from this projection. Such finer details may be stated as

1) A determination of the degree and directions of tilt of the planes of the benzene rings and nitro groups relative to the bc plane.
2) A possible dishing up of the oxygen atoms in the nitro group as was found by R.W.James, G.King and H.Horrocks (8) when determining the structure of para-dinitrobenzene.
3) A possible cant of the NO_2 group with respect to the benzene ring planes.
4) A possible cant of the benzene rings themselves, in other words, does the long axis of the molecule lie in the bc plane.

It is evident then that very little extra information could have been gained if a second projection were made using these redetermined parameters which, as we have seen, agreed very closely with the assumed parameters. We can sum up and say that the bc projection gave a good determination of the y and z parameters, but very little idea of the x parameters beyond the fact that these were not very large because of the approximately regular form of the benzene rings in the projection. For further details about the structure it was necessary to project parallel to a second direction.

When the bc projection was completed and the maxima showed up so clearly, with good agreement between the assumed and determined parameters, the projection was viewed with suspicion.. Many attempts were made to establish good agreement between F(ool) and F(oko) (observed and)

observed and calculated, but this same measure of agreement did not exist for the more general (okl) planes. It seemed at first that we were only getting back again what was assumed in making the projection. The observed values of F(okl) were combined with the calculated phase angles when the Fourier series was evaluated, and it seemed as if a lot of the data used in making the projection just came from the provisionally assumed structure. This accounted for the element of doubt as to how much of what was assumed in making the projection just came back again when the Fourier series was evaluated. This element of doubt was removed when the structure was projected on the ac plane viewed parallel to the b axis and the two projections were found to be consistent.

Testing for a Symmetry Centre of the Molecule.

With this element of doubt still in mind at this stage of the work, it was decided to attempt an independent determination to see if the molecule itself had a centre of symmetry as assumed at the outset of this work. If this turned out to be the case then these determinations would to a certain extent confirm previous results. If we assume the molecule to have a centre of symmetry, the structure factors, as previously calculated, are given by

$$F(hkl) = 4 \cos 2\pi kb \cos 2\pi\left(hx+lz+\frac{k+l}{4}\right) \cos 2\pi\left(ky - \frac{k+l}{4}\right)$$
$$- i\, 4 \sin 2\pi kb \sin 2\pi\left(hx+lz+\frac{k+l}{4}\right) \sin 2\pi\left(ky - \frac{k+l}{4}\right)$$

Considering the (hol) planes only, and remembering that such spectra are present only for even values of l

$$F(hol) = 4 \cos 2\pi(hx+lz).$$

From this it follows that

$$|F(hol)| \text{ is not equal to } |F(\bar{h}ol)|$$

Assuming for the present that all the C and N atoms lie in the (100) crystal planes, an assumption first suggested from packing considerations and later from measurements on the bc projection, where there was evidence of only a small tilt of the benzene ring planes with respect to the (100) crystal plane, then for such atoms our structure factor becomes

$$F(hol) = 4 \cos 2\pi lz.$$

The difference between $|F(hol)|$ and $|F(\bar{h}ol)|$ will, on these assumptions, be due to the twist of the oxygen atoms only, the NO_2 groups being twisted in such a way that the oxygen atoms lie above and, or, below the (100) crystal planes. If no such twist

(exists)

exists on the NO_2 groups it is obvious that $|F(hol)|$ and $|F(\bar{h}ol)|$ will then be identical. Such a possibility, however, has already been eliminated from packing considerations and an examination of the hoo spectra.

If for the present we forget any such information as was obtained from the bc projection, and again suppose the C and N atoms all to lie in the (100) plane, a second possibility arises. The two NO_2 groups of one molecule can now be twisted in opposite directions by the same amount, thus making the molecule non-symmetrical. Working on these assumptions, the structure factors for the C and N atoms will be the same as for the symmetrical molecule, and it remains to calculate the F-factors for the oxygen atoms. Taking one such atom to have co-ordinates (x, y, z) we arrive at the following equivalent positions in the unit cell,

$$\left\{x,\ y,\ z;\ x,\ \bar{y},\ \bar{z}\right\} \quad \text{and} \quad \left\{x,\ y+\tfrac{1}{2},\ z+\tfrac{1}{2};\ x,\ \bar{y}-\tfrac{1}{2},\ \bar{z}-\tfrac{1}{2}\right\}$$

The b shift along the y direction has for the sake of simplicity been left out of these calculations, for finally we are only concerned with the (hol) planes. For this atom and its equivalent

$$F(hkl) = e^{2\pi i(hx+ky+lz)}\left\{1+e^{2\pi i\frac{(k+l)}{2}}\right\} + e^{2\pi i(hx-ky-lz)}\left\{1+e^{-2\pi i\frac{(k+l)}{2}}\right\}$$

Considering only spectra of the form hol, i.e. $k=o$, and remembering that such spectra are present only for l even,

$$F(hol) \quad 2e^{2\pi i(hx+lz)} + 2e^{2\pi i(hx-lz)}$$

or

$$A = 4\cos 2\pi hx \cos 2\pi lz$$

$$B = 4i \sin 2\pi hx \cos 2\pi lz.$$

(similarly)

Similarly for the second atom having co-ordinates $(\bar{x}, y_1, z_1)$

$$A = 4 \cos 2\pi hx \cos 2\pi lz_1$$

$$B = -4 i \sin 2\pi hx \cos 2\pi lz_1$$

Since $|F(hol)|^2 = A^2 + B^2$, it is evident that in the case of the non-symmetrical molecule

$$|F(hol)| = |F(\bar{h}ol)|$$

If then we assume the benzene rings in the molecule to be coplanar with all the C and N atoms lying in the (i00) crystal planes, we have two cases to consider.

1) The NO_2 groups are twisted by the same amount and in the same direction giving a symmetrical molecule. In this case $|F(hol)|$ and $|F(\bar{h}ol)|$ are not equal.

2) The NO_2 groups are twisted by the same amount but in opposite directions giving rise to a non-symmetrical molecule. In this latter case $|F(hol)|$ and $|F(\bar{h}ol)|$ are identical.

It was necessary now to test for this agreement or difference in structure factors for corresponding hol and $\bar{h}$ol reflections. The small crystal, previously used in the intensity determinations of the ool and oko reflections, was rotated about its b axis. It was at this stage of the work that the only available Cu tube ceased to function, and all subsequent exposures with this particular compound were taken with characteristic Fe radiation. The wavelength of Fe $k\alpha_1$ 1.932 A and of Fe $k\alpha_2$ = 1.936 A. The mean value λ = 1.934 A was used, and the reciprocal lattice nets modified accordingly. Using the 50 degree cam the position for the crystal axes, relative to the incident X-ray beam, was calculated to record all the spectra given below, if present, on

(the same)

the same film.

$\bar{1}0\bar{2}$, $\bar{1}0\bar{4}$, $\bar{2}0\bar{2}$, $\bar{2}0\bar{4}$, $\bar{2}0\bar{6}$, $\bar{2}0\bar{8}$, $\bar{2}0\bar{1}\bar{0}$, $\bar{2}0\bar{1}\bar{2}$, $\bar{1}0\bar{1}\bar{0}$ on the L.H.S.

$10\bar{2}$, $10\bar{4}$, $20\bar{2}$, $20\bar{4}$, $20\bar{6}$, $20\bar{8}$, $20\bar{1}\bar{0}$, $20\bar{1}\bar{2}$, $10\bar{1}\bar{0}$ on the R.H.S.

It was found from the reciprocal lattice net determinations that all such spectra could be recorded, if present, when the X-rays were parallel to the c axis of the crystal, and the crystal oscillated through 25 degrees on either side of the c axis. When this film was developed a mere visual inspection of the densities of the spots recorded was enough to indicate a very marked difference between corresponding $\bar{h}o\bar{l}$ and $ho\bar{l}$ spectra.

In a few cases (102, 204, 206,) the difference in density between corresponding $\bar{h}o\bar{l}$ and $ho\bar{l}$ spots was very great, and it seemed hardly possible for the oxygen atoms alone to cause such big differences. We have assumed all the C and N atoms to lie in the (100) crystal planes, that is to say the x co-ordinates for all such atoms must on this assumption be zero, so that the difference between $|F(\bar{h}o\bar{l})|$ and $|F(ho\bar{l})|$ will be determined entirely by the scattering from the oxygen atoms. These differences, however, were so great for the above mentioned spectra that, even if the oxygen atoms scattered completely in phase with the C and N atoms in the direction $ho\bar{l}$ and completely out of phase in the corresponding direction $\bar{h}o\bar{l}$, it seemed hardly possible to account for the big differences in the intensities of these corresponding reflections.

The big differences in the intensity of corresponding $ho\bar{l}$ and $\bar{h}o\bar{l}$ spectra suggested a tilt of the benzene rings so that all the C atoms did not lie in the (100) crystal planes. In other

(words)

words the x co-ordinates for the carbon, and probably the nitrogen atoms, were not zero, which meant that the structure factors of the $(\bar{h}o\bar{l})$ and $(ho\bar{l})$ planes would be different for these atoms. Such a tilt of the benzene rings raken together with a twist on the nitro groups may then account for the big intensity differences observed for corresponding $ho\bar{l}$ and $\bar{h}o\bar{l}$ spectra. The above intensity observations seemed to confirm the results obtained from the bc projection in so far as both gave indications of a probable tilt of the benzene rings.

We can sum up and say that although these experiments give no absolute proof of the existence of a symmetry centre for the molecule, the results are not inconsistent with the assumptions that such a symmetry centre exists. The observations show further that a twist of the NO_2 groups only is not sufficient to account for the big intensity differences between certain corresponding $\bar{h}o\bar{l}$ and $ho\bar{l}$ reflections, and suggest that the benzene rings themselves are tilted out of the (100) crystal planes. In what follows we shall assume the existence of a symmetry centre for the molecule as all the observations so far are consistent with such an assumption.

FOURIER SYNTHESIS OF THE ac PROJECTION.

Intensity Determinations for the hol Reflections.

To obtain further details of this structure, and to serve as a check on the bc projection, it was necessary to project the structure parallel to a second direction. It is obvious from the bc projection, fig.11., that neither along the b nor along the c direction can any clear resolution of the atoms be hoped for. We have seen that the molecule itself probably has a centre of symmetry, which means that a possible twist on the two nitro groups in one molecule must be in the same direction. If there exists any appreciable twist on the NO_2 groups, atoms marked O_8 and $\bar{O}_8$ in adjacent molecules in the bc key diagram (fig. 12) will stand clear if we project the structure parallel to b, or as we shall call it, on the ac plane. If we project parallel to c then, on account of the b shift of the molecule from the origin, such a projection cannot possibly have a centre of symmetry, and the Fourier analysis in this case will follow lines similar to those described for the bc projection. It is evident from structure factor calculations for the (hol) planes (see page 93.) that, if the molecule itself is centro-symmetrical, the structure projected parallel to b will have a centre of symmetry and the Fourier analysis will be easier to handle. For the above reasons it was decided to project the structure parallel to b which for convenience we shall call the ac projection.

To project the structure on the ac face it was necessary to measure the intensities of all the hol spectra, occurring from

(reflections)

reflections of crystal planes round the zone [010]. The crystal used for these determinations was the one previously used for determining the intensities of the ool and oko spectra, and for testing the symmetry of the molecule. This crystal had the shape of a small cube with the edges less than 0.2 mm., so that absorption effects could be neglected to the degree of accuracy with which the intensities could be observed. For the necessary oscillation photographs the 50 degree cam was very suitable, diminishing to a large extent the number of photographs to be taken. By choosing the proper directions of the crystal axes with respect to the incident X-ray beam, considerable overlapping of spectra on successive films was obtained. An example of two such successive films, giving the spectra that could appear if present, is given below

Film 11. L.H.S. all 20ℓ, 302, 304, 306, 308, 100, 200, $10\bar{2}$

R.H.S. all $\bar{1}0\ell$, 0012, 0014, $\bar{2}06$, $\bar{2}08$, $\bar{2}010$

Film 12. L.H.S. all 20ℓ, 102, 1012

R.H.S. all $\bar{1}0\ell$, $\bar{2}0\ell$, 0014

Taking these two films together a good mean factor could be determined by using the common $20\underset{\sim}{\ell}$ and $\bar{1}0\underset{\sim}{\ell}$ spectra, hence the intensities of all spectra recorded on these two films could be expressed on the same scale. Several films were taken until each hol spectrum was given by at least four independent determinations. By a method similar to that used for the okl spectra, all the intensities on these films were expressed on the same scale, and the mean values were taken to represent the final

(intensities)

intensities.

Owing to the glide plane only spectra of the form hol with l even were present, and as the a axis of the crystal was small (3.77 A) and the wavelength used comparatively long, the highest value for h was only 3, and the number of spectra recorded was small. This small number of spectra must lead to serious imperfections in the density distribution of the electrons on this projection. In representing any crystal structure by means of a Fourier series, we must remember that the series is only convergent because the coefficients of the higher terms decrease in magnitude. At larger angles of glancing incidence there is greater interference among the scattered beams, and the values of F, and so the coefficients in the series, become smaller for terms involving high indices. In practice we cannot go on measuring the coefficients of the series indefinitely - a limit is set by the experimental conditions, particularly by the wavelength of the radiation used. If the coefficients of the Fourier series are still large when terminated by experimental conditions, serious defects taking the form of false detail and regions of negative density which have no physical counterpart in atomic structures can be expected. Iron radiation has a comparatively long wavelength for this kind of work and the F values must still have appreciable values when terminated by the experimental conditions, so that a certain amount of false detail was to be expected in this projection.

The following table gives the values of the intensities, I, finally obtained for all the hol spectra recorded. The big differences in intensity for corresponding hol and $\bar{h}ol$ spectra in some cases is very striking.

(table)

Index	I (sec.)	Index	I (sec.)	Index	I (sec.)
100	55.1	106	4.7	208	3.3
200	-	$\bar{1}06$	61.5	$\bar{2}08$	-
300	2.4	108	20.8	2010	3.8
002	78.6	$\bar{1}08$	4.5	$\bar{2}010$	-
004	28.9	1010	15.4	2012	-
006	73.3	$\bar{1}010$	-	$\bar{2}012$	3.3
008	101.0	1012	4.4	302	3.2
0010	5.0	$\bar{1}012$	-	$\bar{3}02$	1.5
0012	-	202	29.1	304	6.3
0014	4.8	$\bar{2}02$	18.4	$\bar{3}04$	-
102	700	204	36.7	306	10.1
$\bar{1}02$	43.3	$\bar{2}04$	4.1	$\bar{3}06$	-
104	172	206	21.9	308	-
$\bar{1}04$	79.4	$\bar{2}06$	3.1	$\bar{3}08$	-

The hol spectra gave an entirely independent set of intensity values for the ool spectra. If these intensity values are compared with the previously determined values of ool from the(okl) planes (see page 66), it is clear that if all the intensities of the hol spectra are multiplied by a factor 4, the two sets of intensity values will then be approximately expressed on the same scale. When trying to establish agreement between F(hol) observed and calculated we can then compare the observed values of F(hol) directly with $\frac{F(hol)\ calculated}{4}$, as was done for the ac projection where spectra of the type okl were used. This multiplication of intensities by a

(factor)

factor 4 was not done directly, the F factors were first calculated from the formula $|F(hol)| = \sqrt{\frac{I\,(hol)}{\phi}}$, and then these F(hol) factors were multiplied by a factor 2. This will explain the presence of the factor 2 in a later table (page 105) which gives the observed and calculated values for F(okl).

The Preliminary Summation Equations.

Substituting h for k in the equations derived earlier (page 78) we get

$$A(oz) = 2\sum_{1}^{L}\{C(ol)\cos lz - S(ol)\sin lz\} + F(ooo)$$

$$A(hz) = 2\sum_{1}^{L}\left[\{C(hl)+C(\bar{h}l)\}\cos lz - \{S(hl)+S(\bar{h}l)\}\sin lz\right] + 2C(ho)$$

$$B(hz) = 2\sum_{1}^{L}\left[\{C(hl)-C(\bar{h}l)\}\sin lz + \{S(hl)-S(\bar{h}l)\}\cos lz\right] + 2S(ho)$$

The ac projection had a centre of symmetry, and the origin of the co-ordinates (x_s o, z_s) was taken at this centre of symmetry when a probable structure was assumed. This centre of symmetry must then apply to each of the component waves which define the structure in the two-dimensional Fourier series given above. Either a peak or a trough of each of these component waves must coincide with the origin which is now also a symmetry centre. The phase angle δ (hol), which measures the displacement of the peak of the wave from the origin, is now limited to values π or 0, and these two cases can be dealt with by making the signs of the coefficients, F(hol), either negative or positive.

In the projection under consideration then all th S(hl) terms vanish, leaving us with simple preliminary summation equations. If we substitute F(hl) for C(hl) in these equations and divide throughout by a factor 4, to reduce the amplitudes of the waves to

(values)

values within the ranges of the values printed on the Beevers strips, $\bar{9}9$ to 99, we are left with the following summations to make

$$\tfrac{1}{4}A(oz) = \sum_{1}^{L} \tfrac{1}{2}F(ol)\cos lz + \tfrac{1}{4}F(ooo)$$

$$\tfrac{1}{4}A(hz) = \sum_{1}^{L} \tfrac{1}{2}\left\{F(hl)+F(\bar{h}l)\right\}\cos lz + \tfrac{1}{2}F(ho)$$

$$\tfrac{1}{4}B(hz) = \sum_{1}^{L} \tfrac{1}{2}\left\{F(hl)-F(\bar{h}l)\right\}\sin lz.$$

and finally

$$\rho(xz) = A(oz) + \sum_{1}^{h} A(hz)\cos hx - \sum_{1}^{h} B(hz)\sin hx.$$

Evaluating the Fourier Series.

The preliminary summations were carried out as for the bc projection. The cell edge corresponding to 1 was again divided into 60 equal parts, so that the values obtained from the strips gave the summation directly for the interval $z=0$ to $z=0.25$. The extension to cover the interval $z=0.25$ to $z=0.50$ can be done easily if we remember that cos lz is symmetrical about $\pi/2$ and sin lz antisymmetrical about $\pi/2$, for even values of l which are the only spectra present in this case. It was not even necessary to make this extension as there were other centres of symmetry by means of which the extension could be accomplished directly. The maximum h index in this summation was only 3, and it was advisable to make the interval of division along this cell edge $\frac{1}{75}$. This was done simply by considering a synthesis of four unit cells to be made, this short edge being considered as quadrupled. Hence all that was done to obtain an interval $\frac{1}{75}$ in the a direction, was to multiply the h indices of the F(hol)

(factors)

factors by 4, and then proceed in the usual way. The strips then gave the projection over the range $x = 0$ to $x = 1.00$ directly. The strips finally gave the projection over one quarter of the unit cell directly, and the area was extended by operation of the symmetry centres in the projection.

The values of F(hol) as calculated from the formula $F \propto \sqrt{I}/\phi$ are given in the following table. The fourth column, F × 2, as explained before, will bring F(hol) and F(okl) on the same scale since it was found, ~~that~~, from considerations of the ool spectra, that $I(okl) \doteqdot 4\ I(hol)$. The values of (F × 2) are then multiplied by a factor 4 and expressed to the nearest whole number. This factor 4 comes from the fact that in the bc projection F(okl) calculated $\doteqdot$ 4 F(okl) observed. These values are those appearing in the fifth column under Final F. When carrying out the preliminary summations the values used were $\frac{\text{Final F}}{2}$.

Index	$\sqrt{\frac{I}{\phi}}$	F (obs.)	F × 2	Final F
100	$\sqrt{\frac{55.1}{4.6}}$	3.46	6.92	28
200	-	-	-	-
300	$\sqrt{\frac{2.4}{1.1}}$	1.48	2.96	12
002	$\sqrt{\frac{78.6}{9.85}}$	2.82	5.64	23
004	$\sqrt{\frac{28.9}{4.7}}$	2.48	4.96	20
006	$\sqrt{\frac{73.3}{2.9}}$	5.03	10.06	40
008	$\sqrt{\frac{101.0}{2.0}}$	7.10	14.20	57
0010	$\sqrt{\frac{5.0}{1.4}}$	1.89	3.78	15

Index	$\sqrt{\frac{I}{\phi}}$	F (obs.)	F × 2	Final F
0012	-	-	-	-
0014	$\sqrt{\frac{4.8}{1.0}}$	2.19	4.38	18
102	$\sqrt{\frac{700}{4.0}}$	13.2	26.4	106
$\bar{1}02$	$\sqrt{\frac{43.3}{4.0}}$	3.29	6.58	26
104	$\sqrt{\frac{172.0}{3.1}}$	7.45	14.90	60
$\bar{1}04$	$\sqrt{\frac{79.4}{3.1}}$	5.05	10.10	40
106	$\sqrt{\frac{4.7}{2.3}}$	1.43	2.86	11
$\bar{1}06$	$\sqrt{\frac{61.5}{2.3}}$	5.17	10.34	41
108	$\sqrt{\frac{20.8}{1.7}}$	3.50	7.00	28
$\bar{1}08$	$\sqrt{\frac{4.5}{1.7}}$	1.63	3.26	13
1010	$\sqrt{\frac{15.4}{1.3}}$	3.46	6.92	28
$\bar{1}010$	-	-	-	-
1012	$\sqrt{\frac{4.4}{1.1}}$	2.00	4.00	16
$\bar{1}012$	-	-	-	-
202	$\sqrt{\frac{29.1}{1.85}}$	3.96	7.92	32
$\bar{2}02$	$\sqrt{\frac{18.4}{1.85}}$	3.16	6.32	25
204	$\sqrt{\frac{36.7}{1.6}}$	4.78	9.56	38
$\bar{2}04$	$\sqrt{\frac{4.1}{1.6}}$	1.60	3.20	13
206	$\sqrt{\frac{21.9}{1.4}}$	3.96	7.92	32
$\bar{2}06$	$\sqrt{\frac{3.1}{1.4}}$	1.49	2.98	12

(cont.)

Index	$\sqrt{\frac{I}{\phi}}$	F (obs.)	F × 2	Final F
208	$\sqrt{\frac{5.3}{1.2}}$	1.66	3.32	13
$\bar{2}08$	-	-	-	-
2010	$\sqrt{\frac{3.8}{1.05}}$	1.90	3.80	15
$\bar{2}010$	-	-	-	-
2012	-	-	-	-
$\bar{2}012$	$\sqrt{\frac{3.3}{1.0}}$	1.82	3.64	15
302	$\sqrt{\frac{3.2}{1.1}}$	1.71	3.42	14
$\bar{3}02$	$\sqrt{\frac{1.5}{1.1}}$	1.17	2.34	9
304	$\sqrt{\frac{6.3}{1.05}}$	2.45	4.90	20
$\bar{3}04$	-	-	-	-
306	$\sqrt{\frac{10.1}{1.0}}$	3.17	6.34	25
$\bar{3}06$	-	-	-	-
308	-	-	-	-
$\bar{3}08$	-	-	-	-

To determine the signs of the coefficients a provisional structure was assumed, and the F factors calculated for such a distribution of atoms. The signs of these calculated F's were then used with the observed values of F(hol), and the series evaluated. As a first approximation it was assumed that the z co-ordinates were fairly accurately known from determinations on the bc projection. The bc projection gave indications of a small tilt of the

(benzene rings)

benzene rings relative to the bc plane, but as we were only dealing with the projected distances, it was impossible to determine from the bc projection the direction of the tilt relative to the crystal axes. Similarly for any twist of the NO_2 groups the direction could not be determined. As a first approximation it was assumed that all the C and N atoms lay in the (100)plane, in other words the x co-ordinates for such atoms were zero. The NO_2 group was assumed to be twisted through an angle of 30 degrees, and the x co-ordinates of the O atoms calculated for such a twist, taking the x co-ordinate of O_8 (fig.12) as negative. With these (x, z) co-ordinates the values of F(hol) were calculated. The agreement between observed and calculated values of F(hol) was very poor, if it could be called agreement at all. Using only the stronger reflections the Fourier series was evaluated, and as was to be expected the projection so obtained showed no resolution of the atoms.

Considering the ac projection so obtained in conjunction with the already determined bc projection (fig 12), it could, to a certain extent, be interpreted. It was evident from these two projections that for one half of the molecule, that marked with the letters C_1, C_2, C_3, C_4, etc., at one corner of the bc projection (fig. 12), the bulk of the scattering material, indicated by the contour lines on the ac projection, was distributed along the positive c direction towards the negative side of the a direction. This will be clear if we refer to fig. 14 which represents the key diagram for the final ac projection shown in fig, 13. Even though no estimate of the values of the x parameters could be obtained from

(the ac)

the ac projection, it was evident that, probably most of the atoms for the half of the molecule under consideration had negative x coordinates. This new information led to some interesting lines of reasoning.

For a few of the more prominent reflections an estimate was made of the values of the F factors, assuming all the atoms in the unit cell to scatter in phase in producing them. This was done by simply summing the atomic scattering factors (fo), appropriate to the angles of scattering, for all the atoms in the unit cell. Of particular interest was the 102 spectrum which had by far the greatest F of all the hol and okl spectra measured, and it was subsequently found that this gave the clue to the ac projection. Going back for a moment to the bc projection, it was previously found that for the strong 008, 0411 and 043 reflections the atoms lay nearly in sheets on the corresponding crystal planes. On this scale of intensity measurement, the (008), (0411) and (043) planes were calculated to scatter approximately 53, 57, and 51 % respectively of the possible maximum in these directions. Here again the great advantages of making absolute determinations cannot be overlooked. Such absolute intensity measurements will give a true value of the percentage of the possible maximum scattered, so that a much more direct and stingent comparison can be carried out. We may find, for instance, that a particular reflection is so strong that its value of F(okl) is very nearly the maximum which could be given if all the atoms were scattering in phase. This shows at once that the atoms are so arranged that they lie in sheete on the (okl) crystal planes.

(the percentage)

The percentage measurements made in the case under examination expressed the percentages on a relative scale, and too much importance could not be attached to the actual numerical values of these scattered percentages. Absolute comparison could not be made between F(okl) observed and calculated and the exact relationship between measured and observed intensities was unknown. The bc projection gave indications of this relationship, since there was fair agreement between F(okl) observed and calculated if the observed okl intensities were multiplied by a factor 4. There is reason to believe then that the determined intensities multiplied by a factor 4 must approach the absolute intensities, and guided by this relationship we can make the necessary comparison between the percentage scattered of the possible maximum for the various planes, without attaching too much importance to the actual numerical values of the scattered percentages. If for example a certain okl reflection is found to scatter 57 % of the possible maximum, and the atoms are found to be nearly arranged in sheets on these (okl) crystal planes, then if any (hol) reflection scatters, say 60 %, of the possible maximum, we can infer that the atoms must again be arranged to lie nearly on these (hol) crystal planes.

Calculations giving the percentage of the possible maximum scattered by certain (hol) planes were made. The 102 reflection was of particular interest, and it was found to scatter 66 % on this scale of measuring intensities. If we compare this value with the values 53, 57, and 51 % given by the 008, 0411 and 043 reflections respectively, it is reasonable to assume that in this ac projection the atoms are roughly distributed in sheets on the

(102) crystal planes. On the other hand the 100, 200, 300 reflections only gave 16, 0, 15 % respectively of the possible maximum along these directions. Considering these facts it was at once obvious that the C and N atoms could not possibly all lie in the (100) plane, which was the arrangement assumed for the first approximation. Even if there were complete interference between the waves scattered by the O atoms and those scattered by the C and N atoms in the hoo direction, the F(hoo) values calculated for such an assumed structure (i.e. C and N atoms all in the (100) plane) were very much higher than the corresponding observed values. The strong reflections given by the planes (102) and (104), 66 and 44 % respectively, and the fact that F(200) was absent, suggested a heavy concentration of electrons between the (102) and (104) planes, in such a way that there was also a maximum distribution at intervals of $(\frac{1}{2}\ a)$ to account for F(200) absent.

To test this line of reasoning a second projection was made, the (x, o, z) co-ordinates being determined as follows. On a large sheet of graph paper the z co-ordinates, as determined from the bc projection, of one molecule and its equivalent given by the glide plane condition were plotted. The a and c axes were drawn to scale, and traces of the (102), (104) and (200) lattice planes drawn on this plane diagram. It was at once apparent from this diagram that if all the atoms plotted along the c direction with their proper z co-ordinates as determined from the bc projection, were displaced along the $\bar{a}$ direction until they all came on a plane between the (104) and (102) planes, but closer to the (102) plane, there was also heavy distribution of scattering material

(at intervals)

at intervals of roughly $\frac{1}{2}$ a. With all the atoms lying in this plane their x co-ordinates were calculated graphically. It must be pointed out that such an atomic distribution at once destroyed the hitherto assumed symmetry of the molecule, and that the projection obtained by using these parameters will not be a true representation of the projection of the actual structure on this ac plane. The main aim in making this projection was to test the validity of the structure derived from such considerations as previously given. In other words does such an atomic arrangement give better agreement between F(hol) observed and calculated, in so far as spectra calculated to be strong were really observed to be strong. If this turned out to be the case then the atomic distribution must be near the truth, and by making redeterminations on the resulting projection a better set of parameters can be obtained. In a projection of this nature the signs of the Fourier coefficients can only be positive or negative. If then this assumed structure is near the truth, the signs for the larger coefficients will be correct, and as we are using these signs with the observed F(hol) values the projection that follows, if we use only these larger coefficients, will tend to square things up automatically and give results nearer the truth.

With such an atomic distribution as given above the F(hol) values were calculated. The agreement between F(hol) observed and calculated was very much better than for the first approximation where all the C and N atoms were assumed to have zero x co-ordinates. A large number of the coefficients changed sign, and the series was evaluated for the second time using these corrected signs. In the projection so obtained there was no resolution of any one atom,

(but when)

but when taken together with the bc projection it could be clearly interpreted and there were no inconsistencies. With the atoms as numbered in the key diagram,fig. 12., and considering only one half of a molecule at the corner of this projection, atoms 1, 5, and6 were overlapping near the origin, then followed a region of comparatively low electron density, followed by an oval-shaped heavy distribution due to atoms 2, 3, 4, 7 and 9 all overlapping in the ac projection. Again there was a region of comparatively low electron density followed by a third maxima which was interpreted as two oxygen atoms O_8 and $\bar{O}_8$ from neighbouring molecules coming exactly behind one another. The contour diagram gave no indications of a possible position for any one atom, but it was clear that, for this half of the molecule, the scattering material was off the (100) plane in the $\bar{x}$ direction. Further investigation showed that, taking the assumed symmetry of the molecule itself into account, such a distribution of atoms could not be accounted for by a tilt of the benzene rings so long as we assume the long axis of the molecule to lie in the (100) plane. The contour diagram suggested a small cant on the molecule as a whole in the $\bar{x}$ direction. In other words the long axis of the molecule was inclined to the (100) plane at a small angle. From the bc projection there was no evidence of such a cant of the molecule, which, if appreciable, should have been indicated as a shortening of the long axis on the bc projection. For the ac and bc projections to be consistent we must infer then that such a cant cannot be very big.

With this information, and making our measurements from the O_8 and $\bar{O}_8$ maximum on the ac projection, a probable position was

(found)

found for atom N_7 in the oval-shaped distributiom. This was done by using the previously assumed distance O - N, taking the z co-ordinate of N_7 as determined from the bc projection. Assuming the molecule to have a centre of symmetry and that the benzene rings were co-planar, a plane model of the molecule was constructed to the same scale as used in the ac and bc projections, the dimensions of the benzene rings being those assumed in the preliminary structure. This plane model was placed in a position to coincide with a corner molecule of the bc projection (fig. 12). The model was then given various degrees of tilt and cant until the x co-ordinates, calculated from the various degrees of tilt and cant of the plane model, when plotted on the ac projection came at positions likely to give an electron density distribution similar to that indicated by the contour lines on the ac projection. The positions of the atoms were plotted for these calculated x values using as z co-ordinates the values determined from the bc projection. The atomic distribution obtained in this way suggested only a small angle between the long axis of the molecule and the bc plane, and it seemed as if the ac amd bc projections were consistent as far as this angle of cant was concerned.

The (x, o, z) co-ordinates determined in this way conformed to the assumed symmetry of the molecule keeping the benzene rings in the same plane and might be expected to give an electron distribution approximating to that indicated by the contour lines on the second ac projection. These new parameter values were used to calculate the signs of the Fourier coefficients, and the series was

(evaluated)

evaluated for the third time using all the observed reflections. A few coefficients changed sign and the agreement between F(hol) observed and calculated, although still far from satisfactory, was much better than in the previous ac projection. The plane model of the molecule was again used in a similar way with this third ac contour diagram and new estimations of the x parameters were made. The x co-ordinates changed only slightly. The Fourier series was evaluated for the fourth time, using these redetermined parameters. Only a few of the weaker coefficients now changed sign, and the projection that followed was hardly any different from the previous one.

To obtain better agreement between F(okl) observed and calculated, a fifth and final projection was made. Accurate determinations of the x parameters were made by considering the fourth projection and the plane model together as previously described. The parameters so determined changed very slightly, and when the F(hol) values were calculated from these final parameters, only F($\bar{2}$08) changed sign, going from a small positive to a small negative value, but as F($\bar{2}$08) observed was zero this made no difference in summing the series, so that the projections obtained for the fourth and fifth attempts were exactly the same. This final projection showed that no resolution of any one atom could ever be obtained. Since the exact positions of the atoms would never show as maxima on this projection nothing more could be done about it. We can go on guessing the parameters until final agreement is established between the values of F(hkl) observed and calculated, but the molecule has so many degrees of freedom and there are so many

(possibilities)

possibilities that this becomes an improfitable task, especially when the exact relationship between calculated and experimentally determined intensities is not accurately known. The bc projection gave an approximate relation between F(okl) observed and calculated, in so far as there was general agreement when the observed values of F(okl) multiplied by a factor 4 were compared with the calculated structure factors. This approximate relation ship was a great help in making the ac projection. There was now something substantial to work on, and we could change our assumed structure until the numerical values of F(hol) calculated approached the values 4×F(hol) observed.

When the bc projection was started the relation between F(okl) observed and calculated was not known, and the great difficulty was to establish an approximate relationship . This had to be done by altering the assumed structure until there was the same general rising and falling off of intensities for the various (okl) planes in both the calculated and experimentally determined intensity values. This question of the exact relationship between calculated and observed intensities represents the fundamental difficulty in this work, and the advantages of making absolute intensity determinations, where the exact relation between observed and calculated intensity values is known, cannot be stressed sufficiently.

We can sum up and say that the final x parameters depend on agreement between the observed and calculated intensities of the hol spectra, and are not fixed by the ac projection. This serves rather as a guide to the tilt of the benzene ring and nitro groups.

(the assumption)

The assumption is made throughout the work on the ac projection that all the carbon atoms in the molecule lie in the same plane, and the best agreement between observed and calculated intensities consistent with this assumption is sought. The position of the nitrogen and oxygen atoms influence the hol intensities considerably. The degrees of freedom are the two angles fixing the plane of the benzene rings, and the x co-ordinates of oxygen and nitrogen, and the number is thus still considerable . The various degrees of tilt of the molecule necessary to give final agreement between F(hol) observed and calculated will be discussed under the section dealing with the description of the molecule.

The contour lines on the final ac projection were drawn at intervals 100, 150, 200, and 250, the 275 contour being the dotted line. As in the case of the bc projection the final summations made gave the values $\frac{1}{4}\int(xz)$, and to express these contour lines in electrons per A^2 we must multiply the values of $\int(xz)$ on this projection by 4, and divide by the area of the ac face. The outer contour line will then represent $\frac{400}{3.77 \times 15.39} = 6.90$ electrons per A^2, with the contours at intervals of 3.45 electrons per A^2. The dotted line in this case is the 18.98 electron contour. The contour diagram drawn from the final values of $\int(xz)$ for the projection on the ac face, viewed parallel to b, is shown in fig.13. This contour diagram may be interpreted with the help of the key diagram, fig.14, which shows the structure projected on the ac face.

The final parameters based on, but not fixed by, this ac projection are given below in table B. Then follows a table showing the agreement found between F(hol) observed and calculated. The

(values)

values of F(hol) observed in this latter table are given as they were determined experimentally, the F(hol) calculated values being divided by a factor 4 to make the comparison direct.

TABLE B.

Atom	x in A	z in A
C1	- 0.10	0.39
C2	- 0.66	1.73
C3	- 0.82	2.45
C4	- 0.40	1.78
C5	0.17	0.47
C6	0.34	- 0.28
N7	- 1.16	2.55
O8	- 1.63	3.60
O9	- 0.75	2.05

Index	$\frac{\sin\theta}{\lambda}$	F (obs.)	F (calc.)
100	.133	6.9	11.9
200	.265	-	-1.2
300	.398	3.0	-2.8
002	.065	5.6	2.5
004	.130	4.9	-3.5
006	.195	10.1	8.4
008	.260	14.2	12.2
0010	.325	3.8	-4.3
0012	.390	-	0.4
0014	.455	4.4	-4.0

(cont.)

Index	$\frac{\sin\theta}{\lambda}$	F (obs.)	F (calc.)
102	.148	26.4	36.1
$\bar{1}02$	.148	6.6	-3.7
104	.186	14.9	-8.5
$\bar{1}04$	.186	10.1	3.4
106	.236	2.8	-0.4
$\bar{1}06$	.236	10.3	13.3
108	.292	7.0	8.3
$\bar{1}08$	.292	3.3	-1.4
1010	.351	6.9	7.9
$\bar{1}010$	.351	-	-0.2
1012	.412	4.0	-6.5
$\bar{1}012$	.412	-	-3.1
202	.273	7.9	9.5
$\bar{2}02$	.273	6.3	-1.2
204	.295	9.6	16.1
$\bar{2}04$	.295	3.2	9.0
206	.329	7.9	-9.9
$\bar{2}06$	.329	3.0	1.7
208	.372	3.3	2.3
$\bar{2}08$	.372	-	-0.5
2010	.420	3.8	6.8
$\bar{2}010$	.420	-	-1.4
2012	.472	-	2.5
$\bar{2}012$	.472	3.6	-5.7
302	.403	3.4	0.7
$\bar{3}02$	.403	2.3	4.0

(cont.)

Index	$\frac{\sin\Theta}{\lambda}$	F (obs.)	F (calc.)
304	.419	4.9	7.4
$\bar{3}04$	.419	-	2.8
306	.443	6.3	5.8
$\bar{3}06$	.443	-	-0.1
308	.475	-	-0.8
$\bar{3}08$	.475	-	0.1

Considerations from the ac and bc Projections.

Considering the results obtained from these two projections it is evident that very little extra information can be gained by projecting parallel to c or on the ab plane. If we view the bc projection along c, it is clear that in a projection on the ab face there will be considerable overlapping of the atoms. The area of this face is only (3.77×9.56) A^2 as compared to (3.77×15.39) A^2 for the ac face, so that we can expect even less resolution than in the ac projection. Not a single atom will stand clear in this projection, and, as in the case of the ac projection, there will be no way of determining the parameters directly from the contour diagram. Furthermore a projection of the structure on the ab face cannot have symmetry centres, and this will complicate matters a great deal and further limit the degree of accuracy that can be obtained. Also the only available radiation was from an Fe tube. Such radiation was found not to be very suitable for this kind of work as the coefficients in the Fourier series were terminated by experimental conditions when their values were still appreciable. For the above

(reasons)

reasons it is evident that this was all that could be done to determine the structure of the crystal.

No corrections for absorption-effects were made in the intensity determinations. With the tiny crystals used such effects were calculated to be very small, and the degree of accuracy to which the intensities were measured did not justify making small corrections for absorption.

The temperature factor does not enter the expressions used for determining the observed intensities. In making these projections we are chiefly concerned with the experimentally determined electron distributions which already include the thermal displacements. In the ac projection the phase angles are either 0 or π and the magnitude of the Fourier series coefficients are experimentally determined, hence for this projection no correction for the temperature factor is necessary. In the bc projection the magnitude of the Fourier coefficients are still determined by experiment, but the phase angles are calculated from an assumed structure and should accordingly be corrected for the thermal movements of the electrons. In a crystal of this nature the thermal movements will be mainly inter-molecular, the atoms in each molecule are held by firm bonds so that intra-molecular movements will be small. All our calculated structure factors came from parameters assumed for a single molecule so that the errors due to temperature effects are probably not greater than the possible errors in the intensity determinations.

Description of the Molecule.

Corresponding atoms in the unit cell are marked in the same way in all key diagrams.(fig.s 12 and 14) The carbon atoms linked to the nitro groups are denoted by C4 and $\bar{C}4$, the CH units by C2, $\bar{C}2$; C3, $\bar{C}3$; C5, $\bar{C}5$; C6, $\bar{C}6$; the carbon to carbon link between the two benzene rings by C1, $\bar{C}1$, the nitrogen atoms by N7, $\bar{N}7$ and the oxygen atoms by 08, $\bar{0}8$; 09, $\bar{0}9$. We assume each molecule to have a symmetry centre midway between the two benzene rings, which are supposed to be co-planar. The bar in the above mentioned atoms denotes inversion across the symmetry centre of the molecule. Table C to follow gives the values of the parameters as finally determined from the ac and bc projections in the way already described. The bc projection showed very clear maxima and the values of y and z in table C come from determinations on this projection, the x parameters being based on the ac projection which gave no check on the z parameters. All the parameters in table C are expressed in A units, taking the corner of the unit cell marked 0 in the key diagrams, fig. 12, 14, as origin.

TABLE C.

Atom	x A	y A	z A
C1	-0.10	0.34	0.38
C2	-0.66	0.57	1.73
C3	-0.82	1.75	2.46
C4	-0.40	2.90	1.79
C5	0.17	2.92	0.47
C6	0.34	1.68	-0.28
N7	-1.16	4.18	2.54

(cont.)

Atom	x A	y A	z A
O8	-1.63	4.15	3.60
O9	-0.75	4.93	2.05
$\bar{C}1$	0.10	-0.82	-0.40
$\bar{C}2$	0.66	-0.87	-1.68
$\bar{C}3$	0.82	-2.05	-2.43
$\bar{C}4$	0.40	-3.22	-1.71
$\bar{C}5$	-0.17	-3.18	-0.44
$\bar{C}6$	-0.34	-1.91	0.35
$\bar{N}7$	1.16	-4.33	-2.50
$\bar{O}8$	1.63	-4.53	-3.65
$\bar{O}9$	0.75	-5.42	-2.01

The dimensions of the molecule as calculated from these parameters are as follows:

C1 - C2 = 1.48 A,	$\bar{C}1 - \bar{C}2 = 1.40$ A.
C2 - C3 = 1.39 A,	$\bar{C}2 - \bar{C}3 = 1.41$ A
C3 - C4 = 1.40 A,	$\bar{C}3 - \bar{C}4 = 1.44$ A.
C4 - C5 = 1.44 A,	$\bar{C}4 - \bar{C}5 = 1.39$ A.
C5 - C6 = 1.47 A,	$\bar{C}5 - \bar{C}6 = 1.50$ A.
C6 - C1 = 1.56 A,	$\bar{C}6 - \bar{C}1 = 1.39$ A.
C1 - $\bar{C}1$ = 1.42 A,	
C4 - N7 = 1.67 A,	$\bar{C}4 - \bar{N}7 = 1.56$ A.
N7 - O8 = 1.16 A,	$\bar{N}7 - \bar{O}8 = 1.26$ A.
N7 - O9 = 1.00 A,	$\bar{N}7 - \bar{O}9 = 2.27$ A.
O8 - O9 = 1.95 A,	$\bar{O}8 - \bar{O}9 = 2.06$ A.

The molecule almost certainly has a centre of symmetry which implies that corresponding links as given above should be equal. Considering the bc projection (fig. 12) and following the dotted lines on it , it appears as if atoms C1, $\bar{C}4$, $\bar{C}6$ are displaced on the projection. These dotted lines are parallel lines drawn where possible through the centres of all the carbon atoms represented in this diagram by circles. It is evident from the projection that the displacements mentioned are not symmetrical about the symmetry centre of the molecule, suggesting that such displacements of the atoms are not real effects. It must be pointed out at this stage that for both these projections, and particularly for the bc projection, there were regions of comparatively high negative density. Such regions of negative density have no physical meaning and show that a certain amount of false detail can be expected from the projections, and it will be hard to say whether a small displacement of any one atom in the projection is a real effect or simply an effect due to experimental errors, or to the existence of false detail round such regions of the projection. It is significant to note that the C - C links involving atoms C_1, $\bar{C}_4$ and $\bar{C}_6$ are considerably higher than the values of the C - C links given by the undistorted atoms which have values ranging from 1.39 to 1.44 A. R.W.James, G.King and H.Horrocks (8) found the benzene ring in para-dinitrobenzene to be slightly distorted, but it seems probable that the distortions of the benzene ring found in this work were not real effects as they lay near the limits of experimental errors. If we discard the values given by C_1, $\bar{C}_4$, and $\bar{C}_6$ for the C - C links and take a mean value of the rest of the C - C links which all lie

(between)

between 1.39 and 1.44 A, we get a value C - C = 1.41 A. This value agrees well with the value 1.42 A found by Dhar (12) for diphenyl, and with values obtained by other workers on aromatic compounds, in which the benzene ring always approaches a regular hexagon of side 1.40 A. In this work certain carbon atoms appeared to be displaced from their positions in a regular hexagon. It has been pointed out that such displacements are almost certainly due to experimental errors and for further calculations we shall regard the benzene ring as a regular hexagon of side 1.41 A.

The C - C link between rings comes to 1.42 A as compared to Dhars (12) value of 1.48 A in diphenyl. Atom C_1 appears to be displaced in the bc projection, the distortion being in such a direction as to shorten this $C_1 - \bar{C}_1$ link, but we shall use this value of 1.42 A for our further calculations. The mean $C_4 - N_7$ link comes to 1.61 A, and is considerably greater than the value 1.53 A found by R.W.James, G.King and H.Horrocks (8) for para-dinitrobenzene. In the bc projection, fig. 11, $\bar{N}_7$ is clearly resolved whereas N_7 is not so clearly defined, and it will probably be better if we take the value 1.56 A given by the distance $\bar{C}_4 - N_7$ as our mean link. The distances N - O are very different, probably again because N_7 and O_9 are not clearly resolved, and all we can do is to take the mean values $N_7 - O_8 = 1.21$ A and $N_7 - O_9 = 1.14$ A. This gives an effect similar to that found by James, King and Horrocks in the above reference where such a shortening, amounting to the same order, was observed for the distances N - O. For our final determinations we shall consider the benzene rings to be regular hexagons with the dimensions of the molecule as follows

C - C aromatic = 1.41 A.

C - C between rings = 1.42 A.

C - N = 1.56 A.

$N_7 - O_8$ = 1.21 A.

$N_7 - O_9$ = 1.14 A.

$O_8 - O_9$ = 2.00 A

The key diagram for the bc projection (fig. 12) indicates clearly the shift of the molecule from the origin 0, the symmetry centre of a molecule at the corner of this projection having co-ordinates (0, -0.16, 0) with respect to 0. This shift of 0.16 A corresponds to an angular co-ordinate of 6 degrees, which agrees well with the value 7 degrees estimated in the provisional structure. Measurements on the bc projection show that the molecules pack in such a way that the projections of the long axes, $C_4 - \bar{C}_4$, on the bc plane make angles of 30 degrees with the b axis. This again agrees well with the value 30 degrees assumed in the provisional structure.

The Tilt of the Plane of the Benzene Rings.

We consider one of the two molecules in the unit cell, that whose centre of symmetry lies near the point 0, fig. 12, chosen as origin of co-ordinates. For considering the orientation of this particular molecule it is convenient to choose new co-ordinate axes fixed relative to the plane of the benzene rings; and to consider how these axes must be orientated with respect to the original a, b, c axes. We take the new origin at I, fig. 15, the centre of symmetry of the molecule, whose co-ordinates relative to the a, b, c axes are (0, -0.16, 0). Let us call the new axes, which are rectangular, ξ, η, ζ. The axis ξ is normal to the plane of the benzene rings and

(in the)

in the positive direction of the a axis. The axis η is the direction IC_4, along the long axis of the molecule, and the axis ζ is at right angles to IC_4 and in the plane of the rings. Using the bc projection (see fig.s 12, 15) we may assume as a first approximation that the ξ axis lies parallel to the a axis, and the η and ζ axes lie in the bc plane, the η axis being rotated away from the b axis through an angle of 30 degrees towards the positive direction of the c axis.

When it came to determining the ac projection it was found that this simple assumption could not account for the observed hol intensities, the molecule had to be given various degrees of tilt and cant to establish agreement between F(hol) observed and calculated. The angles of tilt and cant, determined by trial in a manner already described in the ac projection, were found to be 24 and 7 degrees. These angles of tilt on the benzene rings can best be described in the following way. First suppose the plane of the benzene rings to be rotated about the η axis, IC_4, through an angle of 24 degrees in such a direction as to depress the positive direction of the ζ axis below the bc plane. Those portions of the benzene rings that are so depressed are shaded in fig. 15, the unshaded portions lie above the bc plane after this tilt. Secondly, suppose the η axis, IC_4, to be tilted about an axis through I lying in the bc plane and perpendicular to the η axis through an angle of 7 degrees, in such a direction that the point C_4, in the positive direction of η, is displaced below the bc plane in the negative direction of a. The projection of IC_4 on the bc plane is not altered by either of these tilts. The projection of lines such as C_2C_6, or C_3C_5 which are perpendicular to the η axis will be affected. The angle C_4PC_3 should

(be about)

be about 93 degrees in the bc projection if the benzene ring is a regular hexagon. Those portions of the molecule that are depressed relative to the plane of this figure by the second tilt are shown with dotted outlines in fig. 15. In this figure throughout, the dotted outlines refer to depression produced by the tilt of the long axis of the molecule relative to the plane bc, and the shading to depression produced by the 24 degree tilt of the molecule about the long axis. Since the molecule has a symmetry centre the unshaded portions and undotted outlines represent corresponding elevations. The depression and elevation of the second molecule in the unit cell are at once obtained by considering the action of the glide planes (010) at intervals $\frac{1}{4}b$ and $\frac{3}{4}b$ and are also shown in fig. 15. The angle of tilt of the benzene ring planes about the long axis of the molecule can be determined independently from the bc projection. It has already been pointed out that in this projection certain carbon atoms appeared to be displaced from their positions in a regular hexagon, such displacements being probably due to experimental errors. It is evident then that determinations of the angle of tilt from this projection cannot be accurate, and can only serve as an approximate check on previous results. The angle of tilt determined from the bc projection using the co-ordinates as given in table C_A (page 121) came to 21 degrees; which is consistent with the value 24 degrees previously described.

In the bc projection, fig. 12, the nitrogen atoms lie very nearly in the same line as the long axis $C_4\bar{C}_4$. This will be evident if we study the dotted lines on this diagram. The nitrogen atoms therefore lie in a plane through $C_4\bar{C}_4$ that is perpendicular to the bc plane. Calculations from the x, y, z parameters for C_4 and N_7 show (that the)

that the link $C_4 - N_7$ makes an angle of about 22 degrees with the ζ axis, or $C_4\bar{C}_4$, the deviation being in the negative direction of the a axis. The line joining the two oxygen atoms O_8 and O_9 is nearly parallel to the plane of the benzene rings but lies at a distance of about 0.44A below it in the negative direction of a.

To describe the actual configuration of the molecule it is convenient to express the atomic co-ordinates in terms of the axes ξ, ζ, ς; ξ being perpendicular to the plane of the benzene rings and through the centre of symmetry I, ζ along the direction of the long axis IC_4 and ς at right angles to this. If x'y'z' are axes parallel to xyz, or the a, b, c translations of the unit cell, but having the point I (x = 0, y = -0.16, z = 0) as origin, so that x' = x, y' = y + 0.16, z' = z.

The equations giving the transformation of the co-ordinates are

$$\xi = x'\cos(\xi x) + y'\cos(\xi y) + z'\cos(\xi z)$$
$$\zeta = x'\cos(\zeta x) + y'\cos(\zeta y) + z'\cos(\zeta z)$$
$$\varsigma = x'\cos(\varsigma x) + y'\cos(\varsigma y) + z'\cos(\varsigma z)$$

With the values of the angles of tilt and cant of the benzene ring planes previously given, the numerical values of the coefficients are as shown in equations (A).

$$\left.\begin{aligned} \xi &= +0.9067\ x' - 0.1094\ y' + 0.4079\ z' \\ \zeta &= -0.1219\ x' + 0.8597\ y' + 0.4963\ z' \\ \varsigma &= -0.4037\ x' - 0.4987\ y' + 0.7670\ z' \end{aligned}\right\} \text{----(A).}$$

Using the parameters given in table C (page 131) these equations give the following values, shown in table D, for the atomic co-ordinates with respect to the ξ, ζ, ς axes. The ζ and ς values for the carbon atoms in the molecule are not shown in table D. It has been pointed

(out at)

out at an earlier stage that, within the errors of experiment, the benzene ring in the molecule approaches a regular hexagon of side 1.41 A. For our calculations we assumed the benzene ring planes to lie in the $\eta\zeta$ plane, an assumption on which the agreement between F(hol) observed and calculated was based. On this assumption we should expect the ξ values for the carbon atoms as given in table D to be zero. These ξ values were calculated from the atomic co-ordinates given in table C which again were derived from the ac and bc projections. The deviation from zero for the ξ values of the carbon atoms in table D are small, such deviations lying within the limits of experimental errors.

TABLE D.

Atom	ξ in A units	η in A units	ζ in A units
C_1	.009		
$\bar{C}_1$	-.0003		
C_2	.028		
$\bar{C}_2$	-.009		
C_3	.051		
$\bar{C}_3$	-.041		
C_4	.033		
$\bar{C}_4$	.000		
C_5	.009		
$\bar{C}_5$	-.003		
C_6	-.007		
$\bar{C}_6$	.026		
N_7	-0.491	5.134	0.252
$\bar{N}_7$	0.488	-4.967	-0.301

(cont.)

Atom	ξ in A units	η in A units	ζ in A units
O_8	-0.481	5.691	1.271
$\bar{O}_8$	0.467	-5.768	-1.279
O_9	-0.401	5.484	-0.663
$\bar{O}_9$	0.436	-5.612	0.778

We have assumed the molecule to have a centre of symmetry, an assumption which was found to be consistent with the results obtained throughout the course of this research. On this assumption we should expect corresponding atoms, say O_8 and $\bar{O}_8$, to have the same numerical ξ, η, ζ co-ordinates. The discrepancies found in table D are probably mainly due to experimental errors, in particular the determinations of intensities. The displacements of certain atoms in the projections have already been pointed out. It seems reasonable to assume that the best values for the parameters in table D will be those giving the numerical mean between the values of corresponding atoms. Assuming the benzene rings to be regular hexagons of side 1.41 A, with their planes lying accurately in the $\eta\zeta$ plane, that is to say ξ for all such atoms is zero, and using the mean ξ, η, ζ, co-ordinates for the corresponding nitrogen and oxygen atoms in the molecule, the results are plotted in plan (projected on the $\eta\zeta$ plane), and in elevation (projected on the $\xi\eta$ plane) in figs 16(a) and 16(b) respectively.

The angles of tilt of the benzene rings, the ξ, η, ζ co-ordinates, together with the links previously given fix all the atoms in this molecule as a unit of the structure.

PACKING OF THE MOLECULES IN THE STRUCTURE.

We must finally consider how a number of molecules such as the one we have described pack together to form the crystal structure. This we shall do in two stages. Firstly we shall consider the linkages between adjacent molecules lying in the same bc plane, and secondly the linkages between molecules in adjacent bc planes. For brevity we shall refer to linkages of the first type mentioned as P linkages and to linkages of the second type as Q linkages.

We must now refer to fig. 17 to study the linkages between adjacent molecules lying in the same bc plane. The diagram represents the structure projected on the bc plane viewed parallel to a. The projection of the unit cell is shown in the diagram, indicating the directions of the b and c axes. We shall refer to molecules at the corners of the unit cells as A molecules. The other molecules, derived from the A molecules by the action of the glide planes, we shall call B molecules. Two such molecules are marked A and B in this diagram. The closest distance of approach between neighbouring oxygen atoms is of the order 4.4 to 4.6 A. These links are those given by the atoms $O_g - \bar{O}_q$, $\bar{O}_g - O_q$, $O_q - \bar{O}_q$ in this diagram (fig. 17). These distances are much greater than the distances of closest approach of oxygen atoms in inorganic structures, which are of the order of 2.7 A, and this indicates at once that the linkages holding the structure together in the directions we are considering are not mainly oxygen to oxygen. There are, however, a number of close links between O and CH units in adjacent molecules and these probably represent the main binding of the structure. We must distinguish between two distinct types of

(O - CH linkages)

O - CH linkages, those between adjacent A or between adjacent B molecules shown in this diagram by the dotted lines $\bar{O}_9C_6$, $\bar{O}_9C_5$, $O_9\bar{C}_6$, $O_9\bar{C}_5$, and those between adjacent A and B molecules indicated by the dotted lines $\bar{O}_8C_3$, $\bar{O}_8C_2$, $O_8\bar{C}_3$, $O_8\bar{C}_2$. We shall first consider links of the type O_9 - CH, i.e. links between neighbouring A or neighbouring B molecules. Linkages of the type $O_9 - \bar{C}_6$, $O_9 - \bar{C}_5$ and their corresponding atoms gave four different values, these four values all lying between 2.94 A and 3.20 A. We should expect corresponding links such as $O_9 - \bar{C}_6$ and $\bar{O}_9 - C_6$ to have the same value considering the symmetry of the molecule itself, and regarding the whole crystal structure as forming a static system on account of these binding forces. The actual values found for $O_9 - \bar{C}_6$ and $\bar{O}_9 - C_6$ were 3.20 and 3.04 A respectively, giving the same order of difference as that found between links of the type $O_9 - \bar{C}_6$ and $O_9 - \bar{C}_5$. We have already seen that certain carbon atoms appeared to be displaced from their positions in a regular hexagon in the bc projection. These displacements, as already pointed out, are almost certainly due to experimental errors, and may account for such differences as were calculated for the O_9 - CH links. It seems reasonable to assume that the molecules in the structure will tend to pack so that all links of the type O_9 - CH approach the same value. The fact that the difference between corresponding O_9 - CH links and links given by $O_9 - \bar{C}_6$ and $O_9 - \bar{C}_5$ are of the same order of magnitude, while the actual values $O_9 - \bar{C}_6$ and $O_9 - \bar{C}_5$ are also of the same order seems to strengthen the above assumption. It appears then that the four values given by the links $O_9 - \bar{C}_6$, $O_9 - \bar{C}_5$ and their corresponding atoms really all approach the same value, and we shall take the mean of these four

(values)

values to represent the distance of closest approach between O and CH units in neighbouring A or neighbouring B molecules. This mean value comes to 3.01 A.

We must next consider the O - CH links between adjacent A and B molecules in the same bc plane, i.e. links of the type $O_8 - \bar{C}_3$, $O_8 - \bar{C}_3$, $\bar{O}_8 - C_3$, $\bar{O}_8 - C_2$ shown in fig. 17. These links have values ranging from3.36 to 3.64 A. The order of difference between these links is the same as that for the O_9 - CH links between adjacent A molecules. Here again corresponding links given by $\bar{O}_8 - C_2$ and $O_8 - \bar{C}_2$ have values 3.36 to 3.64 A and on account of the symmetry of the molecule we should expect such corresponding links to be equal. Following a similar line of argument as for the O_9 -CH links we can again say that all such O_8 - CH links between adjacent A and B molecules will probably approach the same value. In this case the mean O_8 - CH value comes to 3.51 A, and we shall use this value to represent the distance of closest approach between O and CH units in adjacent A and B molecules. It must be pointed out that we are carrying our observations and calculations beyond experimental evidence in calling these links equal, even though there are certain arguments that seem to make this assumption reasonable. It is quite definite, however, that we are dealing with two distinct types of O - CH linkages, since the difference between these two types of linkages appears to be greater than will be allowed by experimental errors. The O - CH links between adjacent A or between adjacent B molecules in the bc plane are shorter than the corresponding links between adjacent A and B molecules in the same plane, the distances being given by 3.01 and 3.51 A respectively. This seems to suggest

(that)

that the binding forces between molecules of the same type are stronger than the forces holding the A and B molecules together. In addition to these O - CH links between adjacent A or adjacent B molecules we also have a number of close CH - CH linkages. Such links are indicated in this diagram (fig. 17) by the full lines between atoms marked C_5 and $\bar{C}_5$. These CH units approach to within 3.60 A of one another. This value can be compared with the value 3.60 to 3.72 A for naphthalene, and 3.77 to 3.80 A for anthracene, obtained by Robertson (22); 3.42 A obtained by Iball (23) for chrysene, and 3.63 A obtained by James, King and Horrocks (8) for para-dinitrobenzene. Finally then if we refer to the molecule marked B in this diagram, we see there are eight links of the type O - CH where such units approach to within 3.01 A of one another. There are also eight links of the type O - CH where the closest distance of approach is 3.51 A. In addition to all these O - CH links we have two links of the type CH - CH where such units approach to within 3.60 A of one another. The O - CH links appear to be the main forces holding the structure together in this bc plane. Any one molecule is linked to neighbouring molecules by sixteen such O - CH links, all such units approaching to within 3.51 A or less of one another. These values 3.01 and 3.51 A can be compared with the values 3.33 and 3.42 A found by James, King and Horrocks (8) for the distances of closest approach between neighbouring O and CH units in para-dinitrobenzene.

The structure appears to be firmly held together by these O - CH links in the directions we have so far considered, and there remains to see what forces hold the molecules in adjacent bc planes together.

(For this)

For this we shall refer to fig. 14 which represents the structure projected on the ac plane viewed parallel to b. We shall again refer to A and B molecules, two such molecules are marked in the diagram. We have already seen that the a spacing of the crystal is only 3.77 A, and from this it at once follows that adjacent CH units in molecules of the type A or B approach to within this value of one another. Similarly the NO_2 groups approach one another to within 3.77 A. If for the moment we consider two such A molecules lying immediately above one another, indicated by the letters A_1 and A_2 in this diagram, we find further possible binding forces. The links we shall refer to now are not joined by lines as in the previous case, but we shall imply the same idea of closest approach when referring to a link say, $O_8 - C_2$. The distance of closest approach between oxygen atoms in molecules A_1 and A_2 is given by the link $O_9 - O_8$ which comes to 3.37 A. This value is greater than the value 2.7 A found in inorganic structures. The links $O_8 - C_3$, $O_9 - C_5$ and their corresponding links approach the value 3.90 A which is greater than the values 3.01 and 3.51 A previously found. The links $O_8 - C_2$ and $O_9 - C_6$ are of the order 4.86 A. These differences between $O_8 - C_3$ and $O_8 - C_2$ are to be expected from the way the molecules are tilted about the $C_4\bar{C}_4$ axes. There are close links between N_7 and O_8 and their corresponding atoms in two such adjacent A_1, A_2 molecules. The values $O_8 - N_7$ come to 3.46 A and these, with the other links mentioned above, probably represent the main binding forces between adjacent A_1 and A_2 or adjacent B_1 and B_2 molecules.

We must now examine the existence of any close links between A and B molecules lying in adjacent bc planes. For this we shall

(refer)

refer to the two molecules marked A_2 and B_1 in fig. 14. Here again we find close linkages between O and CH units. The links $O_8 - \bar{C}_2$, $O_8 - \bar{C}_3$, $\bar{O}_8 - C_2$ and $\bar{O}_8 - C_3$ have values lying between 2.88 and 3.42 A. Corresponding O - CH links, given by $O_8 - \bar{C}_2$ and $\bar{O}_8 - C_2$, have values 3.24 and 2.88 A respectively. Considering the symmetry of the molecules and the fact that the order of difference between these O_8 - CH links is of the same magnitude as previously found for the O - CH links between molecules lying in the same bc plane, we can again say that all such O - CH links between molecules marked A_2 and B_1 (fig.14) probably approach the same value, and use as our distance of closest approach the mean of all the $O_8 - \bar{C}_2$, $O_8 - \bar{C}_3$, $\bar{O}_8 - C_2$ and $\bar{O}_8 - C_3$ links. This mean O_8 - CH value comes to 3.10 A which can be compared with the value 3.01 A previously calculated for links of the type O_9 - CH between adjacent A or adjacent B molecules lying in the same bc plane.

We return now to fig. 17 to see whether there exist any close O - CH links between two adjacent A molecules in this diagram when we consider one such molecule to lie 3.77 A in the a direction above the other. Such linkages involve atoms O_9, C_5, C_6 and their corresponding atoms in what we have called the Q linkages. These O_9-CH links were found to be of the order of 4.47 A, so that there exist no close O - CH links between such adjacent molecules. The reason for these rather long O - CH links lies in the various degrees of tilt and cant of the molecules packed in the structure. The tilts of the benzene ring planes and NO_2 groups are in such directions as to make close O - CH links between adjacent A and B molecules lying in adjacent bc planes. The directions of the angles of tilt then

(imply)

imply that such close O - CH links cannot exist between adjacent A molecules situated at two near corners of the unit cell in the bc plane but separated by 3.77 A in the a direction. This point will be clear if we refer to fig. 15 which shows the elevation and depression of certain sections of the molecule.

It seems probable that these O - CH linkages, or as we have termed Q linkages, are mainly responsible for holding the structure together in the directions considered, i.e. between molecules in adjacent bc planes. There are in addition a number of close links between CH - CH units and between O and N atoms which may be responsible for a considerable part of the binding forces in these directions.

We have already seen that for molecules lying in the same bc plane there are two types of O - CH linkages, those between adjacent A and B molecules where the link O - CH approaches the value 3.51 A, and those between adjacent A or adjacent B molecules where the link O - CH = 3.01 A. We have also seen that the O - CH link between A and B molecules in adjacent bc planes is of the order 3.10 A. These short O - CH links, i.e. 3.10 and 3.01 A, seem to be mainly responsible for holding the A and B molecules together in the structure. It is perhaps significant to point out that in one case these short O - CH links are between adjacent A or adjacent B molecules in the bc plane, and in the other case between adjacent A and B molecules, the molecules in the latter case being separated by the a spacing. These short O - CH links form a system of zig-zag chains in the structure and are probably the main forces responsible for preventing the molecules from sliding or slipping in any direction.

To sum up, every oxygen atom of the type O_g approaches to

(within)

within 3.51 A or less of 6 CH units, two such close approaches are between molecules in the same bc plane, and four are between molecules in adjacent bc planes. Every oxygen atom of the type O_q approaches to within 3.01 A of two CH units. Each NO_2 group, considered as a unit, thus makes eight such close contacts.

We have used the term link between O and CH in a purely geometrical sense, as denoting the distance of close approach of the atoms. It seems likely that such O - CH links are responsible for a considerable part of the forces binding the crystal together. The whole structure is a very compact one, the crystal has a fairly high density, 1.45 grm./cc. and is, for an organic crystal, comparatively hard, and it is tempting to associate these properties with this type of linkage. It is possible that there are appreciable forces between adjacent NO_2 groups, which, as we have seen, approach to within 3.4 A of one another.

SUMMARY.

This crystal, 4 : 4'- Dinitrodiphenyl $C_{12}H_8(NO_2)_2$, is a very interesting example of one which is structurally monoclinic but which can for practical purposes be referred to orthogonal axes. The orthogonal axes may not be crystallographically the most suitable axes that could have been chosen. It will be clear if we study the way the molecules pack in the ac projection (fig. 14.) that the a and c axes can be chosen in such a way that the monoclinic angle will be much greater than 90 degrees. We saw at the outset of this work that, although orthogonal axes could be chosen, space did not allow two such molecules to pack into the unit cell so as to conform to orthorhombic symmetry. To determine the structure the method of double Fourier synthesis has been applied. Projections of the electron density on two axial planes parallel to two axial directions have been made, and the 27 independent parameters have been measured. The space-group is Pc, and the unit cell contains two molecules. The space-group does not make it necessary for the molecule to have a symmetry centre, but such a symmetry centre almost certainly exists. Absolute intensity determinations could not be made and the disadvantages that this entails have already been pointed out, and cannot be sufficiently stressed when accurate determinations of such a complex crystal without a symmetry centre are necessary. The fact that the absolute relation ship between F(hkl) observed and calculated was not known can be regarded as the fundamental difficulty in this analysis, and must be mainly responsible for the displacements found in the projections. All such displacements have already been pointed out and discussed.

(We can)

We can sum up and say that within the errors of experiment the benzene ring approaches a regular hexagon of side 1.41 A, the two rings in the molecule being co-planar with a common axis. The C - C link between rings is 1.42 A. This value is probably on the short side as one of these atoms appear to be displaced on the bc projection in such a way as to shorten this link. The C - N link does not lie in the plane of the benzene rings but is inclined to the long axis of the molecule at an angle of about 22 degrees, the projected distances of the long axes and the C - N links on the bc plane being along the same straight line. The N - O distances are not quite equal, being 1.14 and 1.21 A. The O - O distance is 2.00 A. The line joining O and O in the NO_2 group is nearly parallel to the plane of the benzene rings. The closest approach between O and CH units in adjacent molecules is 3.01 A, and between CH and CH units 3.60 A. A discussion of the packing of the molecules in the structure has been given.

THE UNIT CELL AND SPACE - GROUP OF LEUCODRIN ($C_{15}H_{16}O_8$)

Preparation and Crystallography.

Leucadendron

Leucodrin was first isolated from the leaves of L.Concinnum by Meiring - Beck (24). The organic chemist at the University of Cape Town, Dr. W.S.Rapson, obtained very beautiful crystals on crystallisation. The crystals are transparent white in colour, most of them having a long dagger-shaped form. The smaller crystals were very clear and free from flaws, with two brilliantly reflecting flat,convex faces. When examined under polarised light they showed brilliant colours. On rotation of the nicols they showed straight extinction, showing at once that the crystal had orthogonal axes. As only the two convex faces developed, no goniometer measurements could be made.

Determination of the Unit Cell.

A series of rotation photographs with Cu $k\alpha$ radiation showed complete symmetry for the top and corresponding bottom layer-lines about the centres of the films. On the photographs both layer- and row-lines were clearly defined. Measurements on the films gave the following values for the rectangular lattice-cell translations

$a = 25.27$ A, $b = 8.98$ A, $c = 6.06$ A.

The molecular weight of the molecule is 324.1 on the scale O = 16, and the density was found to be 1.55 - 1.56 gms./cc. Assuming the density, D, to be 1.55 gms./cc, then if n is the number of molecules per unit cell

$$D = \frac{n \times 324.1 \times 1.65}{25.27 \times 8.98 \times 6.06} = 1.55 \text{ gms./cc.}$$

$$\therefore n = 3.98$$

We therefore have four molecules to the unit cell which gives the true density as 1.557 gms./cc.

From the above data the three reciprocal lattice nets were drawn, and films taken about the a, b, and c axes were indexed with the aid of Bernal charts. A very large number of spectra were recorded on the rotation photographs. All such spots could be identified, and for every spot there was a corresponding point on the reciprocal lattice net, and a set of Miller indices could be assigned to each of these spots. To bring in the high order spectra, or spectra scattered through big angles, it was often found necessary to give long exposures. This resulted in the low order spectra being very strong and very often overexposed, with the β peaks showing up as strong spots, and this often caused a certain amount of ambiguity when indexing the films. These β peaks came on layer-lines themselves, falling below those given by the α peaks and this ambiguity only arose when indexing spectra on the zero layer-line. With experience such β peaks could generally be identified and discarded, but in cases of doubt they were identified as follows. For Cu radiation the ratio $\frac{k\alpha}{k\beta}$ is 0.892. If a certain spot was suspected as being the β peak of a strong α spectrum, the ξ value of this α spot multiplied by the above ratio should then be equal to the ξ value of the β peak as measured with the Bernal chart. Occasionally a β peak was present but not its corresponding α, and in such cases extreme care had to be exercised. This ambiguity can be removed by inspecting the positions of the lunes drawn on the reciprocal net, where the reciprocal lattice point corresponding to a certain $\alpha(hkl)$ spectrum fell outside the lunes and so cannot be recorded, whereas

(its corresponding)

its corresponding β (hkl) fell inside the lunes. The necessary rotation can then be given to bring in both the α and β (hkl) spectra and the film so obtained directly compared with the doubtful one. Fortunately such cases occurred very seldom, and with a little experience the β peaks could as a rule be readily identified from their intensity, position and shape.

For crystals with a small spacing in a certain direction, say from 4 to 10 A units, such ambiguity seldom occurred, for in general no reciprocal lattice point will correspond to the ξ value of a β peak. For small reciprocal spacings, however, where several reciprocal lattice points were nearly equidistant from the origin, the β peaks often proved to be troublesome.

The Space-Group Determination.

The Miller indices (hkl), assigned to all the spectra recorded on the rotation photographs, revealed no systematic absences. All reflections of the general type hkl are present showing that the structure is based on a primitive lattice. Screw axes and glide planes were tested for by examining spectra of the type ool and hol. Spectra of the form okl, hol and hko were present for all values of h, k and l, showing that the space-group had no glide planes.

The operation of a two-fold screw axis is such that there is an apparent halving of the spacing along its direction. Suppose we have a two-fold screw axis parallel to the a translation of the unit cell. This means the a axis is effectively halved. If we start with a point (o,o,o), then by the operation of the screw axis we have another point at $(\frac{1}{2},o,o)$. The structure factor for these two points is given by

$F = f_o(1 + e^{2\pi i\, h/2})$ $\quad f_o$ = atomic scattering factor

$f_o(1 + e^{\pi i h})$.

and this is zero when h is odd.

For spectra of the type hoo then, the corresponding structure factor is zero when k is odd. This is the condition governing a two-fold screw axis.

For the films indexed so far only a few spectra of the form oko were present, and these suggested strongly the presence of screw axes. It was necessary then to test this point properly. Using the a* b* net lunes were drawn to bring in the following spectra 100, 200, 300, 400, 500, 600. The corresponding setting of the crystal, rotating about the c axis, was calculated from the lunes, and an oscillation photograph taken with the crystal in this position. On the film so obtained spectra 200, 400 and 600 were strongly recorded, whereas 300 and 500 were definitely absent. On the film the 100 spectrum came too near the central hole in the film where the incident X-ray beam passed through, for it to be recorded if present.To test for this 100 spectrum the crystal was given a similar rotation,but the spectra were recorded on a flat film at a distance 6 cms. away from the crystal as compared to the usual 3 cms. in the case of cylindrical films. With such an arrangement it was calculated that spectra 100, 200, 300 could be recorded if present. The point where the incident X-ray beam impinged upon the film was located, and a thin strip of lead was stuck to the film at this point. This served to absorb the incident radiation, and so prevent splashing which would otherwise obscure spectra that came close in. The film when developed showed 200 recorded as a strong spot, but 100 and 300 were

(absent)

absent. We can say then that spectra of the form hoo are present only with h even, which means a two-fold screw axis parallel to a.

In a similar manner spectra of the form oko and ool were examined. In this case there was no obscurity as none of these spectra came too close to the central hole in the film. Several films, however, had to be taken to bring in the higher order spectra. Here again spectra of the form oko, ool were present only with k and l even, showing the existence of two-fold screw axes parallel to the b and c unit cell translations.

These observations determine the space-group of leucodrin uniquely. It is a primitive lattice with three two-fold screw axes parallel to the unit cell translations. The symbol is $P2_12_12_1$ in the Hermann-Maugin notation, and the dimensions of the unit cell are

$a = 25.27$ A, $b = 8.98$ A, $c = 6.06$ A.

Leucodrin is a complex molecule with a large number of parameters, and the fact that there are 4 molecules in the unit cell, and 3 two-fold screw axes, makes the determination of its final structure almost impossible, particularly as no absolute intensity determinations could be carried out. Other methods were indicated to decide upon a provisional structure. After consultation with the organic chemist it was decided to introduce two bromine atoms into the molecule, hoping that the intensity of the X-rays scattered by the heavy bromine atoms in certain directions might lead to some important information as to the positions occupied by the bromine atoms in the molecule. If it is found that leucodrin and dibromoleucodrin have the same crystalline structure then important results may follow when comparing the intensities of certain spectra from these two compounds.

(It turned)

It turned out that leucodrin and dibromoleucodrin had the same space-group with a strong resemblance in the unit cell dimensions. This will be clear if we study the space-group and unit cell of Dibromo-leucodrin given in the next section of this work.

A rough comparison of the intensities of certain corresponding spectra was made. The structure, however, appeared to be too complicated, and for the present the work was abandoned at this stage.

SPACE GROUP DETERMINATION OF DIBROMOLEUCODRIN ($C_{15}H_{14}O_8Br_2$)

Preparation and Crystallography.

Leucodrin (6gms.) in methyl alcohol (50 cc.) was treated in the cold with bromine (6.5 gms.) in methyl alcohol (50 cc.). The mixture became warm, and the methyl alcohol and slight access of bromine were then distilled off. The residue crystallised from methyl alcohol in colourless prisms as dibromoleucodrin.

These crystals showed brilliant colours under polarised light. Their external form resembled the long dagger-shaped leucodrin crystals. The crystals were not as clear and free of flaws as the leucodrin crystals, and did not show any brilliantly reflecting faces. The external appearance of these crystals rather resembled an accumulation of a large number of crystal plates packed together with their axes parallel to form the "main crystal". The main crystals always gave single crystal rotation photographs, even though they appeared to be complex when examined under a microscope.

Determination of the Unit Cell.

From the rotation photographs taken with the crystals an interesting point was revealed, in that the crystals did not grow the same way as leucodrin. In this case the b axis was the long elongated axis of this dagger-shaped crystal, whereas this corresponding elongated axis was the c axis in leucodrin. Measurements on the rotation photographs indicated that the axes were orthogonal, the dimensions of the unit cell being given by

$a = 23.42$ A, $b = 10.33$ A, $c = 6.63$ A.

As regards the unit cell then there is a strong resemblance between

(the structure)

the structure of these two compounds. Assuming 4 molecules to the unit cell the density, D, comes to

$$D = \frac{795.3 \times 4}{23.42 \times 10.33 \times 6.63} = 1.98 \text{ gms./cc.}$$

The density of the crystals was determined by the method of flotation. Ethylene bromide of density 2.178 gms./cc. at 20°C was diluted with chloroform of density 1.50 gms./cc., until the crystals just floated in the mixture. The density of the mixture was determined and found to be just under 2.00 gms./cc.

The outstanding feature of dibromoleucodrin is the beautiful rotation photographs it gives. On account of the big spacing along the a direction a large number of spectra were recorded on some films. The layer-and row-lines were so remarkably well defined that these films can well be used as reference films for future illustrations. Fig. 18a and 18b show reprints of two such photographs taken about the a and c axes respectively.

Space - Group Determination.

To determine the space-group, the three reciprocal lattice nets a* b*, b* c*, and a* c* were drawn to the scale 20 cms. represent 1A, and the films were indexed in the usual way. Indexing films for rotation about the b and c axes, involving the use of the a* c* and a* b* reciprocal nets respectively, was a long and tedious process. A very large number of spots were recorded on these films. The a* axis was very small so that several reciprocal lattice points falling inside the lunes were very nearly the same distance from the origin, and it was often very difficult to decide between two such nearly equidistant points when only one of them was recorded on the

(film)

film. Great care was necessary to assign the correct indices to all the spectra recorded on such films, and the spotting took a comparatively long time.

An inspection of the Miller indices revealed no systematic absences for the general (hkl)reflections, and there were no glide plane conditions.A few spectra of the general form hoo again suggested screw axes, and these were tested for in a way similar to that described for leucodrin. The experiments indicated the presence of three two-fold screw axes parallel to the a, b, and c directions. The space-group of Dibromoleucodrin was then determined uniquely. It is based on a primitive orthorhombic lattice with four molecules to the unit cell, and three two-fold screw axes at right angles.

Dibromoleucodrin

Space-group $P2_12_12_1$

Unit cell a = 23.42 A

b = 10.33 A

c = 6.63 A.

THE STRUCTURE OF AMMONIUM - GALLIFLUORIDE $(NH_4)_3\ GaF_6$.

Preparation and Crystallography.

$(NH_4)_3\ GaF_6$ was prepared by Prof. Pugh of the Cape Town University. Hydrated gallium fluoride prepared as described by Pugh (25), freshly distilled ammonia, A.R.Hydrofluoric acid. Exactly equivalent quantities of gallium fluoride and ammonia solution were measured out. The ammonia solution was neutralised, and then slightly acidified with hydrofluoric acid. The gallium fluoride was dissolved in this solution and evaporated to crystallisation. The crystals obtained were re-crystallised two or three times from water containing a trace of hydrofluoric acid.

The great bulk of this crystalline deposit when examined under polarised light showed no colour, suggesting at once a cubic structure. Accurate observations, however, showed that some crystals had very tiny bits stuck to their surfaces giving brilliant colours on rotation of the nicols. These observations suggested the presence, in very small proportions, of some other crystalline form not cubic in structure. The crystalline deposit, supposed to be pure ammonium gallifluoride, was examined under a binocular microscope of magnification ten. Two distinct crystal forms appeared to be present in roughly equal proportions. Both forms assumed octahedra shape and we shall refer to these two forms as crystals belonging to group 1. and group 2.

Crystals belonging to group 1. approached on the average $\frac{1}{5}$ mm.^{3} in volume. They were covered with a whitish deposit, resembling a fine powder. The external form of these crystals generally approached

(distorted)

distorted octahedral shapes. Crystals belonging to the second group were characterised by their perfect octahedral form, with brilliantly reflecting faces. All the crystals falling under group 2. were very small, approaching the limit of the size that could be dealt with in the mounting process.

Determination of the Unit Cell and Space-Group of Crystals belonging to group 2.

Rotation photographs taken with crystals belonging to group 2. revealed that the vast majority of these crystals were complex, giving rise to double and triple groups of spots on the films. Only after several attempts a suitable single crystal, free of flaws, was isolated. This crystal was adjusted to rotate about the [100] zone axis, and a series of oscillation photographs were taken to record all the spectra occurring round this zone. For every film a fifteen degree oscillation was given and 9 films were taken in all, making the necessary allowance for overlapping of certain spectra.

The distribution of the spots on these films, strongly resembled that of the NaCl film previously taken for calibrating the camera. This regular chessboard arrangement of the spots, characteristic of a face-centred lattice, at once suggested that we were dealing with a face-centred cubic lattice. A large number of measurements on the films led to a mean value $\zeta = 0.172$ A for the layer-lines.

Hence $a = \frac{\lambda}{a^*} = 8.95$ A.

The molecular weight of $(NH_4)_3 Ga F_6$ was calculated and found to be 237.8 on the scale O = 16, hence

$$\text{Density} = \frac{1.65 \times 237.8 \times n}{(8.95)} = 0.547 \times n \text{ gms./cc.}$$

Where n is the number of molecules in the unit cell. Assuming n = 4,

(then D)

then D = 2.19 gms./cc, which is in good agreement with the measured density of 2.18 gms./cc.

A reciprocal net of edge 3.44 cms., corresponding to a scale 20 cms. = 1 A, was drawn. All the films taken round this zone axis were indexed in turn, using the Bernal chart method. Every spot occurring on the films could be accounted for and a certain set of Miller indices was assigned to each spot. A systematic inspection of these Miller indices showed that, only spectra with hkl either all even or all odd were present. This is the condition for a face-centred lattice. We conclude then that crystals belonging to group 2. are based on a face-centred cubic lattice, with 4 molecules to the unit cell, the unit cell edge being given by a = 8.95 A.

Crystals belonging to Group 1.

A mere examination of the crystalline deposit under a microscope suggested the presence of two distinct crystal groups. This was a rather hasty conclusion for during the course of this work it was found that the external appearance of a crystal was often very misleading. To draw any conclusions from purely external form considerations was decidedly dangerous, and it was often found to give entirely wrong results. It was necessary then to make an X-ray investigation of the crystals belonging to the first group.

A suitable crystal free from flaws was located and examined under polarised light to makesure that none of this third crystalline substance, that showed colour under polarised light, was present. The crystal was mounted about an important zone axis and a few oscillation photographs taken. Comparing the films so obtained with

(those)

those taken for crystals belonging to group 2, it was at once obvious that this crystal was also based on a face-centred cubic lattice with a different unit cell. Measurements of the layer lines gave a mean value $\zeta = .184$, and hence

$$a = \frac{1.539}{.184} = 8.37 \text{ A.}$$

Using these dimensions a reciprocal lattice net was drawn, and applying the Bernal method it was possible to assign a set of Miller indices to every spot recorded on these photographs. A systematic examination of the Miller indices again indicated that only spectra with hkl either all even or all odd were present. The crystal is then based on a face-centred cubic lattice, the unit cell edge being given by $a = 8.37$ A.

The crystalline deposit supposed to be pure $(NH_4)_3$ Ga F_6 was constituted then of at least two, and possibly three, crystal forms. The two main forms were found to be present in more or less equal proportions, both forms having a cubic structure. Observations under a polarising microscope suggested the presence, in very minute quantities, of a third crystalline form not cubic in structure.

At this stage an attempt was made to determine the composition of this second cubic crystal found to be present as an impurity in $(NH_4)_3$ Ga F_6. Important conclusions followed when certain papers published by Pauling (26), Menzer (27) and Bozorth (28) were referred to.

In 1924 Pauling determined the spacing for the (100) planes in $(NH_4)_3$ Al F_6 and gave $a_o = 8.40$ A, and for $(NH_4)_3$ Fe F_6, $a_o = 9.10$ A. Menzer pointed out this big difference as the ionic radii of Al^{+3} and Fe^{+3} are nearly the same. Menzer gives the following values for $(NH_4)_3$ Al F_6

$a_o = 8.904$ A, $D = 1.837$ gms./cc.

Pauling agrees with these values of Menzer as the crystals he examined were not $(NH_4)_3$ Al F_6 but $(NH_4)_2$ Si F_6. Pauling's values $a_o = 8.40$, $D = 2.02$ gms./cc, agree with Bozorth's values for $(NH_4)_2$Si F_6 given as

$a_o = 8.38$ A, $D = 2.01$ gms./cc.

Pauling further states that the parameter determination is not affected by the incorrectly assumed composition and his value $u = 0.197$ accordingly substantiates Bozorth's value $u = 0.205$ for $(NH_4)_2$ Si F_6.

These results for the structure of $(NH_4)_2$ Si F_6 resemble very closely those of the impurity found present in $(NH_4)_3$ Ga F_6. In what follows it is confirmed that the impurity present was $(NH_4)_2$Si F_6. The spacing of the (100) planes for this impurity was found to be 8.37 A. Assuming the crystal to be $(NH_4)_2$ Si F_6, its molecular weight was found to be 178.1 on the scale O = 16. There are 4 molecules to the unit cell, hence

$$\text{Density} = \frac{1.65 \times 178.1 \times 4}{(8.37)^3} = 2.01 \text{ gms./cc}$$

These results are in good agreement with those given by Bozorth.

The inorganic chemist who prepared this compound was consulted as to the possibility of this impurity being present in the preparation of $(NH_4)_3$ Ga F_6. This turned out to be the case, the silicafluoride arising from the silica present as an impurity in the hydrofluoric acid. A chemical analysis confirmed the impurity as $(NH_4)_2$ Si F_6, as previously interpreted by comparison of the results obtained with those given by Pauling and Bozorth.

There still remained this third crystalline substance, present in minute proportions, to consider.

The Monoclinic Crystal

It was desirous to examine the third impurity, present in small proportions, in the crystalline mixture of $(NH_4)_2\ SiF_6$ and $(NH_4)_3\ GaF_6$. A fresh deposit was prepared by the inorganic chemist. The fresh crystalline deposit when examined under polarised light showed brilliant colours with a complete absence of any cubic form. It appeared then that the compound $(NH_4)_3\ GaF_6$ crystallised in two distinct forms, and that the latter form was the third one present in minute quantities when the deposit was first examined. This assumption could not be tested by comparison, as the impurity in the first deposit was present in far too minute fragments to be handled for the purpose of rotation photographs.

The latter deposit crystallised as very small, but well formed, hexagonal crystals with brilliantly reflecting faces. The hexagonal faces revealed a small slant, suggesting a monoclinic structure. One such crystal, mounted about an axis parallel to the hexagonal faces, gave the following goniometer measurements.

Vernier reading	Angle between normals
336° 30′	
30° 0′	53° 30′
83° 33′	53° 33′
156° 30′	72° 57′
209° 57′	53° 27′
263° 30′	53° 33′
336° 30′	73° 0′

These crystal faces are represented diagramatically in fig. 19. Assuming the crystal to be monoclinic, then by inspecting the symmetry of the crystal, the a and b axes are as indicated in diagram, for these axes are at right angles in a monoclinic crystal. The direction of the crystal axes was verified by examining the crystal under polarised light. It was found that the a face, as determined from symmetry considerations, gave straight extinction when looking down on it through a polarising microscope. This means that the b axis of the crystal, if it is monoclinic, must lie in this (100) plane, showing that the axes were correctly identified.

The first rotation diagram was taken with the crystal rotating about the c axis. The setting was easily accomplished by using the method of reflected light. The crystal gave a very clear photograph. It was at once obvious that the film was not symmetrical about the zero layer-line, revealing a monoclinic nature. Rotation about the a axis also gave a very clear non-symmetrical photograph. For rotation about the b axis a perfectly symmetrical photograph was obtained. From these photographs it was inferred that the crystal was monoclinic, and the next important step was to determine the monoclinic angle.

Determination of the Monoclinic Angle.

The (001) face never developed in these monoclinic crystals so that no direct goniometer measurements could be made to determine the monoclinic angle. Some other scheme had to be tried. One of these monoclinic crystals was mounted about the c axis in such a way that the a and b axes could be adjusted independently with the arcs on the camera. The necessary adjustments were made until perfectly straight layer-lines were obtained when an oscillation photograph was taken.

(With)

With the crystal in this position the vernier readings on both arcs were taken. The position of the crystal was as illustrated in fig. 20. By adjusting one arc only the a direction could be changed without altering the direction of the b axis. By trial and error the necessary adjustments were made until the crystal rotated accurately about the c* axis. The resulting rotation photograph showed row-lines but no layer-lines when a Bernal chart was superposed on it. The readings on the two arcs were again taken for the crystal in the latter position. One arc reading was found to be unchanged, the other moved through 13 degrees. Hence the angle between c and c* is approximately equal to 13 degrees, or the monoclinic angle $\beta \doteqdot 103°$. This gave an approximate estimate of the angle β, and an attempt was now made to determine this angle accurately.

The values ζa, ζb, ζc were determined accurately from the three rotation photographs about the a, b, and c axes. The values of $a = \frac{\lambda}{\zeta a}$, $c = \frac{\lambda}{\zeta c}$ were calculated. For a monoclinic lattice

$$a^* = \frac{\lambda}{a \sin\beta} = \frac{\zeta a}{\sin\beta} \quad \text{and} \quad c^* = \frac{\zeta c}{\sin\beta}$$

Taking the value $\beta = 103°$, the a*, c* axes were calculated, and the a*c* net drawn to scale.

Suppose now the crystal is rotating about the b axis, then for any spot hol on the zero layer-line we have

$$\xi(hol) = \sqrt{h^2 a^{*2} + l^2 c^{*2} + 2hl\, a^*c^* \cos\beta^*}$$

and similarly

$$\xi(h\bar{o}l) = \sqrt{h^2 a^{*2} + l^2 c^{*2} - 2hl\, a^*c^* \cos\beta^*}, \text{ therefore}$$

$$|\xi(hol)|^2 - |\xi(h\bar{o}l)|^2 = 4hl\, a^*c^* \cos\beta^*$$

$$= \frac{4hl\,\xi_a\,\xi_c\cos\beta^*}{\sin^2\beta^*}\text{, hence}$$

$$\frac{\cos\beta^*}{\sin^2\beta^*} = \frac{\left|\xi_{(hol)}\right|^2 - \left|\xi_{(\bar{h}ol)}\right|^2}{4hl\,\xi_a\,\xi_c} \quad \ldots\ldots\ldots (1)$$

On the a*c* net traces of the sphere of reflection were drawn, for a 15 degree oscillation, to bring in the two corresponding reciprocal lattice points, hol and $\bar{h}$ol, whose numerical distances from the origin differed by as large an amount as possible, that is to say two spots near the central region of the film with their ξ values, as measured on a Bernal chart, very different. From the lune considerations the crystal was adjusted to reflect two such corresponding hol and $\bar{h}$ol reflections. Two such spectra were the 402 and $\bar{4}02$ reflections, whose ξ values were 0.847 A and 0.717 A respectively. Substituting these values in equation (1) we have

$$\frac{\cos\beta^*}{\sin^2\beta^*} = \frac{(0.847)^2 - (0.717)^2}{4\times 4\times 2\times 0.175\times 0.154}$$

Assuming values for β^*, the equation was solved by trial. Three independent determinations of the value of β^* were made, each time using a different set of corresponding spectra. The values were found to agree closely, the mean value being $\beta^* = 77°5'$.

This method gave a fairly accurate determination of the monoclinic angle, by first assuming an approximate value for β to identify suitable hol and $\bar{h}$ol spectra. The assumed value of β does not enter the final calculations, all the measurements coming directly from the films. The agreement between these calculated values and the value found by rotation about a reciprocal axis is, however, remarkably good.

The size of the unit cell was finally determined to be

a = 8.79 A, b = 6.31 A, c = 10.00 A, $\beta = 102^{\circ} 55'$.

The monoclinic angle was taken to be accurately known and the a*, b* and c* axes were calculated, and three reciprocal lattice nets drawn. Indexing films for rotation about the b axis was the usual straightforward process. For films taken about the other two axes a little consideration was necessary. To keep the same reciprocal lattice net the direction of the incident radiation had to be changed for the successive reciprocal layers. The process involved has been outlined briefly in the introduction to this work. In this way it was possible to assign a set of Miller indices to every spectrum recorded on the rotation photographs. The crystals were well formed and gave very good and clear photographs. Reproductions of two such films, taken about the a and b axes respectively, are shown in fig.s 21a and 21b. They are typical of a monoclinic structure, indicating clearly the non-symmetrical layer-lines for rotation about the a axis.

A systematic examination of the Miller indices showed that only spectra for which (h + k + l) is even were present. This is the condition governing a body-centred lattice. For a monoclinic lattice the only possible planes of symmetry are those perpendicular to the b axis.

To test for glide planes only spectra of the type hol were important. A system inspection of such spectra revealed that (hol) was present only for (h + k) even. This condition, however, is already embodied in the condition (h + k + l) = 2n governing a body-centred lattice, so that no new information is gained. Similarly the condition for a screw axis parallel to b, i.e. oko present only for even values of k, is a special case of the condition (h + k + l)

(is even)

is even. All we can say is that this monoclinic crystal is based on a body-centred lattice, X-ray analysis giving no information about the symmetry planes or axes of the space-lattice.

When it came to determining the density of this substance, contradictory results were obtained. Assuming the compound to be $(NH_4)_3\ Ga\ F_6$, the molecular weight has been calculated as 237.8 on the scale O = 16.

$$\text{Density} = \left\{ \frac{1.65 \times 237.8}{8.79 \times 6.31 \times 10.00 \times \sin 102°55'} \right\} \times n \text{ gms./cc.}$$

$$= (0.726 \times n) \text{ gms./cc.}$$

where n is the number of molecules per unit cell.

The density of $(NH_4)_3\ Ga\ F_6$, as calculated from the cubic structure, comes to 2.19 gms./cc, the experimentally determined value being D = 2.18 gms./cc. In the above case if n = 3, then the density for this monoclinic form is D = 2.18 gms./cc, which is in good agreement with the other two determinations.

A face-centred monoclinic lattice with three molecules to the unit cell is, however, an impossibility. No such space-group exists, and we must conclude that the crystalline substance present in this monoclinic form cannot be $(NH_4)_3\ Ga\ F_6$. Our earlier interpolation that $(NH_4)_3\ Ga\ F_6$ probably exists in two forms is thus disproved. A possible explanation seems to be that this second impurity, believed to be pure $(NH_4)_3\ Ga\ F_6$, is a hydrated form of ammonium gallifluoride containing an unknown amount of water of crystallisation.

Probable Structure for $(NH_4)_3$ Ga F_6.

The compound $(NH_4)_3$ Ga F_6 is based on a face-centred cubic lattice, the edge of the unit cell being given by a = 8.95 A. There are four molecules in the unit cell. We must dispose of 4 Ga atoms, 12 NH_4-groups and 24 F atoms in a unit cell of dimensions as given above. The space-group on which this structure is based seems to be Fm3. It further appears that the only possibility is for the Ga atoms and NH_4-groups to be arranged on two interpenetrating face-centred cubic lattices, an arrangement similar to that of the Na and Cl atoms in the rocksalt structure. Such an arrangement accounts for 4 Ga atoms and 4 NH_4-groups. From symmetry considerations the remaining 8 NH_4-groups must come at the centres of the eight small cubes into which the unit cell can be subdivided. The Fluorine atoms are arranged as regular octahedra round the Ga atoms with parameters given by uoo, $\bar{u}$oo, ouo, o$\bar{u}$o, oou, oo$\bar{u}$. Such an arrangement will account for the 24 F atoms in the unit cell. The only undetermined parameter in the structure is the distance F to Ga.

Bozorth (28) gives the value 1.72 A as the shortest distance between F and Si atoms in the structure $(NH_4)_2$ Si F_6. This value is the sum of the Goldschmidt radii for Si and F atoms (The Crystalline State Vol.1. page 115 by W.H. and W.L.Bragg.) This distance of closest approach leads to the parameter u = 0.205 determined by Bozorth for the $(NH_4)_2$Si F_6 structure. It seems reasonable to assume that the shortest distance between F and Ga atoms in the $(NH_4)_3$ Ga F_6 structure will also be the sum of the ionic radii, which comes to (0.62+ 1.33) = = 1.95 A, giving a value $u = {}^{1.95}/_{8.95} = 0.218$.

A probable value for the only undetermined parameter in the

$(NH_4)_3 Ga F_6$ structure seems to be given by $u = 0.218$. The order of magnitude of this parameter is the same as for other Ammonium-fluoride compounds whose structures have been determined by Pauling, Menzer and Bozorth (26, 27, 28). Our intensity measurements, however, are too inaccurate to determine this parameter with any great accuracy, and the structure described above, which seems to be the only possible one, must suffice for the present.

In conclusion I wish to express my sincere thanks to professor R.W.James of the Cape Town University for his invaluable suggestions and constant encouragement throughout the course of this research, and in particular for the use of his yet unpublished manuscript which deals with the whole problem of X-ray Diffraction and its Applications to Crystal Structures in a most elegant manner. I am also much indebted to The Research Grant Board of the Union of South Africa for the award of a research grant for part of the time while this work was under investigation.

REFERENCES.

1.	Polanyi M.	Z. Phys. 7,149 (1921)
2.	Ewald P.P.	Handbuch der Physik. 23, 208-476 (1933) Der Aufbau der festen Materie und seine Erforschung durch Röntgenstrahlen.
3.	Bragg W.H. and W.L.	The Crystalline State Vol.1. p.15. (1933)
4.	Bernal J.D.	Proc. Roy. Soc. A, 113, p. 117 (1927)
5.	Bragg W.H. and W.L.	The Crystalline State. Vol1. p. 45 (1933)
6.	Gull and Turner	J. Chem. Soc. of London p.494 (1929)
7.	Henry N.F.M.	Minerological Mag. Vol 25.23 (1938)
8.	R.W.James, G.King, H.Horrocks.	Proc. Roy. Soc. London Vol. 153 p.240 (1935)
9.	Bragg W.H. and W.L.	The Crystalline State Vol.1. p.115 (1933)
10.	Lonsdale K.	Proc. Roy. Soc. A, Vol 123, p. 494 (1929)
11.	Robertson J.M.	Proc. Roy. Soc. A, Vol. 142, p. 659 (1933)
		Proc. Roy. Soc. A, Vol. 162, p. 568 (1937)
		Proc. Roy. Soc. A, Vol. 154, p. 187 (1936)
		Proc. Roy. Soc. A, Vol. 140, p. 79 (1933)
		Proc. Roy. Soc. A, Vol. 118, p. 709 (1928)
		J. Chem. Soc. Jan.(1938) p. 131.
		Science Progress. Vol.22, No. 126 Oct.(1937)
12.	Dhar J.	Indian J. Physics 7, 43 (1932)
13.	Bragg W.H.	Phil. Trans. Roy. Soc. A. 215, 253, (1915)
14.	Duane W.	Proc. Nat. Acad. Science. 9, 159, (1923)
		Proc. Nat. Acad. Science. 11, 489, (1925)
15.	Havighurst R.J.	Physical Review p.1-19, Vol.29, No.1, Jan. (1927)

16. Compton A.H. "X-rays and Electrons" Chap. 5. (1926)

17. Bragg W.L. Proc. Roy. Soc. A, 123, 537 (1929)

18. Robertson J.M. Proc. Roy Soc. A, Vol. 157, p. 79-99, (1936)

19. Robertson J.M. Reports on Progress in Physics, Vol.4, p.332, (1938)

20. R.W.James and G.W.Brindley. Phil. Mag. (7) 12, 81, 729 (1931)

21. Lipson H. and Beevers C.A. Proc. Phys Soc. Vol.48, p. 772, (1936)

22. Robertson J.M. Proc. Roy. Soc. A, Vol.140, p. 79 (1933)

23. Iball J. Proc. Roy. Soc. A, Vol. 146, p. 140, (1934)

24. Meiring-Beck Pharm. J. (1886) 17, 327, 408.

25. Pugh Journal Chem. Soc. 1047, (1930)

26. Pauling L. Z. Kryst. 74, 104, (1930)
J. A. Chem. Soc. Vol 46, 2738, 2743, (1924)

27. Menzer G. Z.Kryst. 73, 113, (1930)

28. Bozorth M. J.A.Chem. Soc. Vol. 44, 1066 (1922).

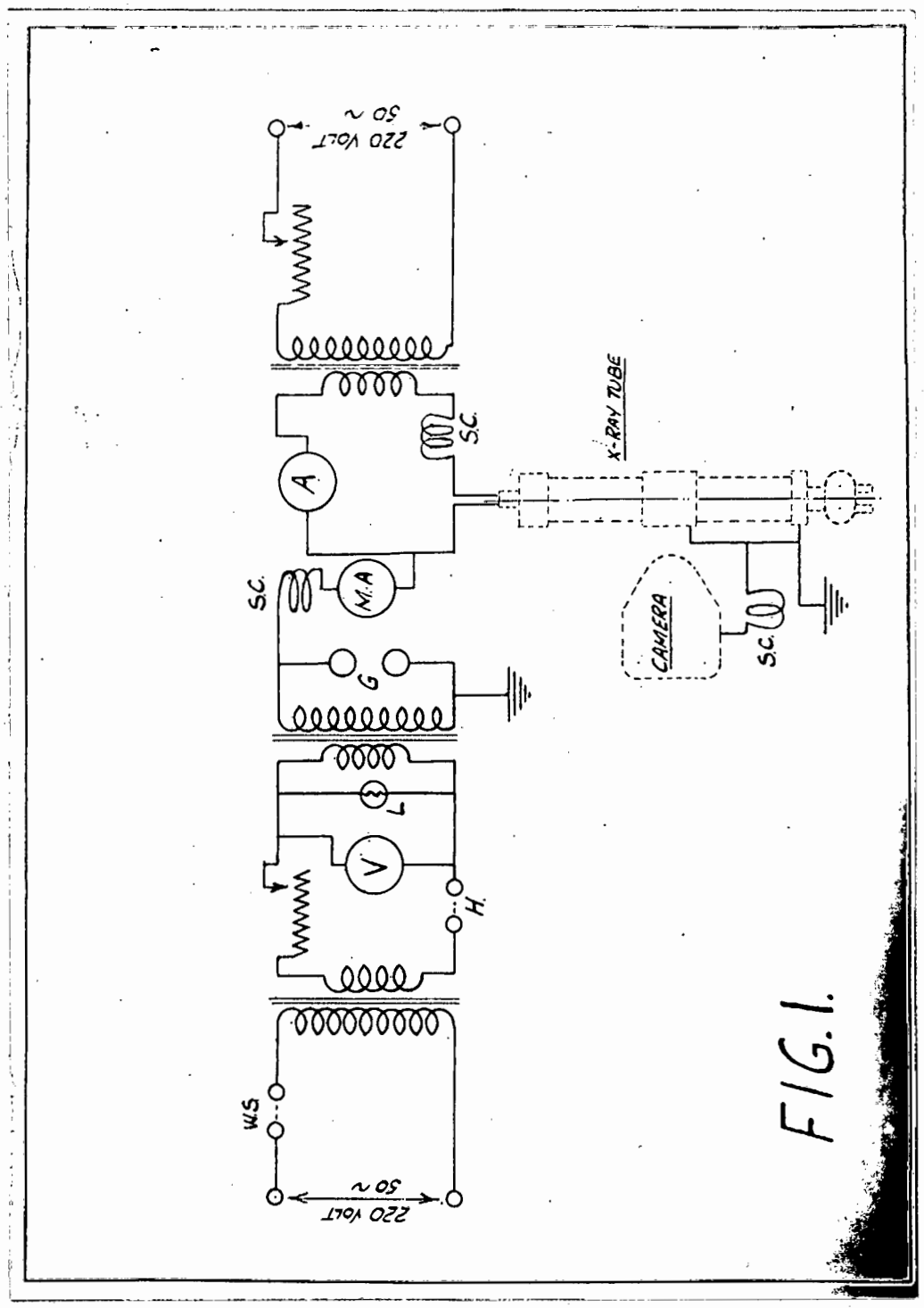

FIG. 1.

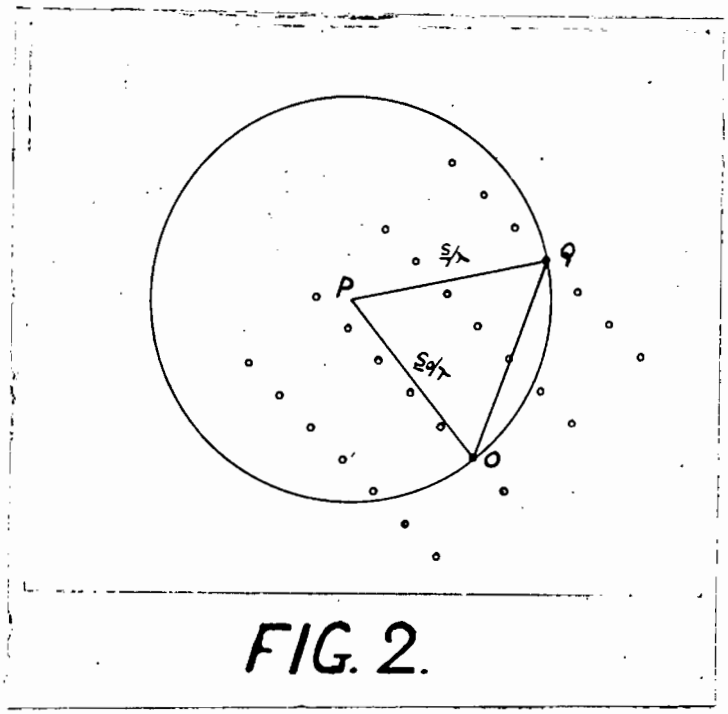

FIG. 2.

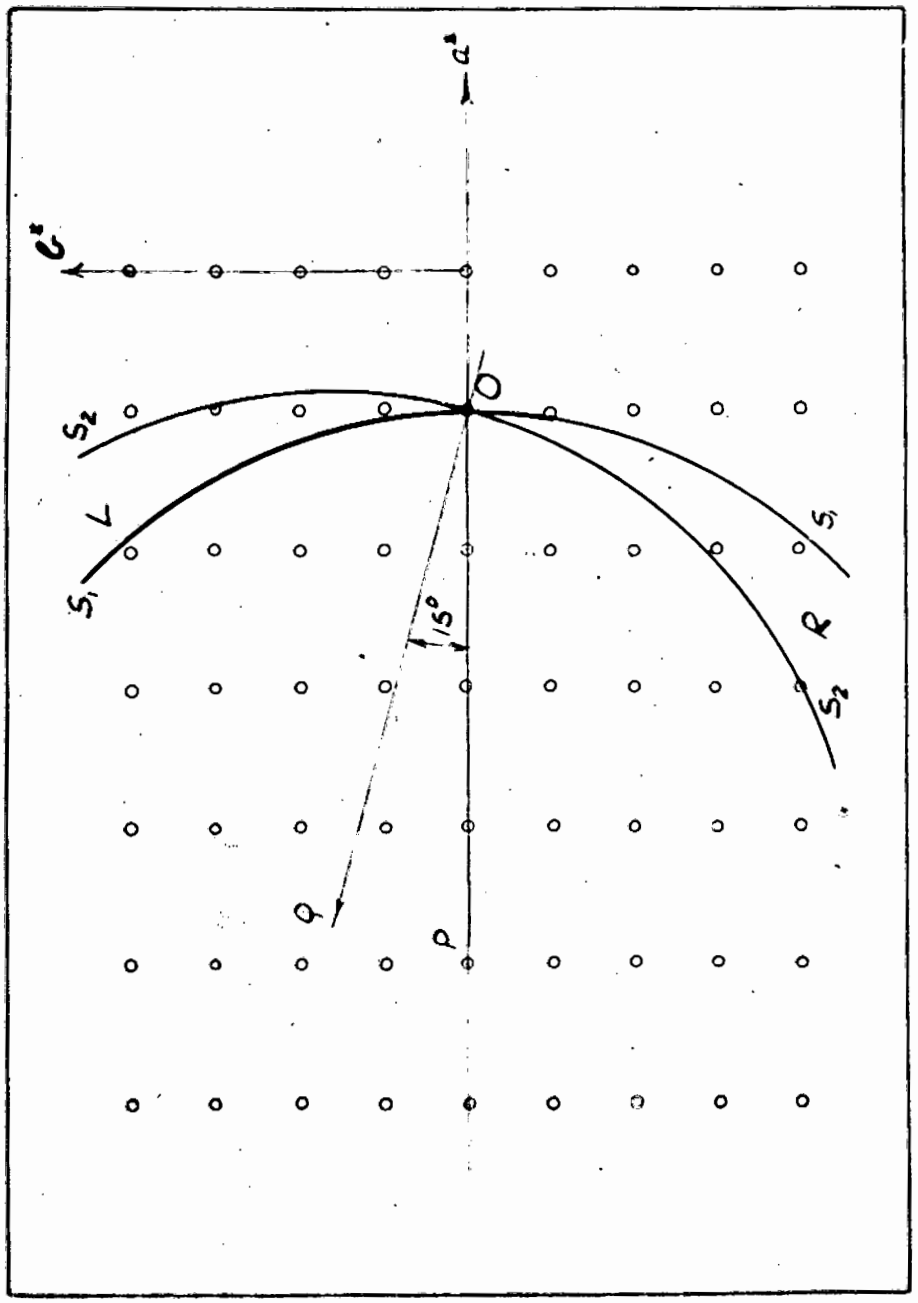

FIG. 3.

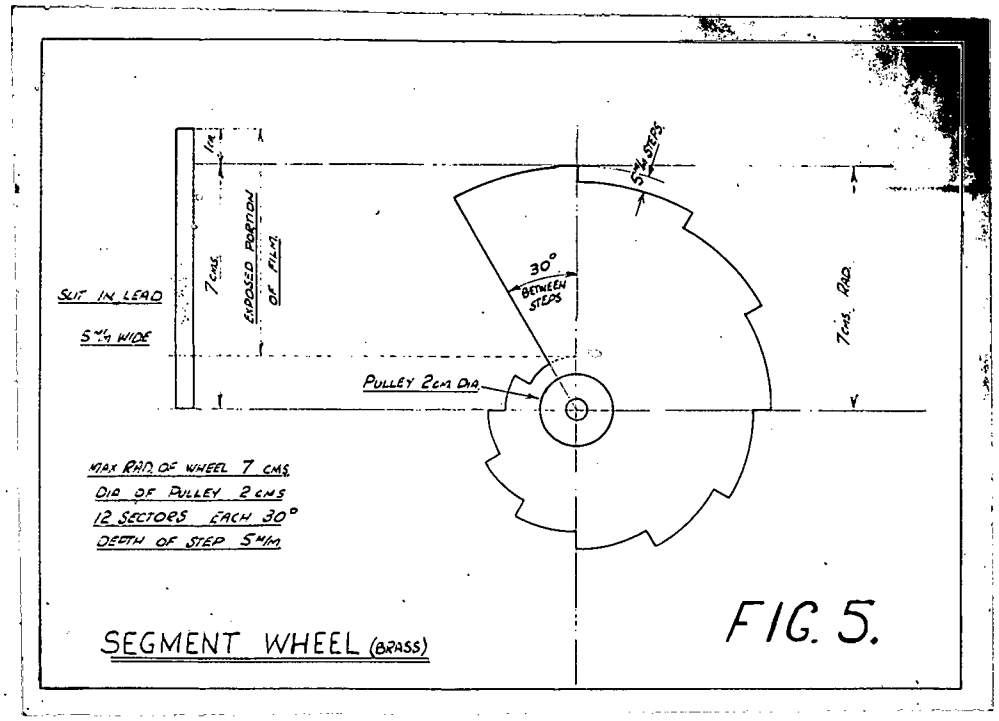
SLIT IN LEAD
5 m/m WIDE
7 cms.
EXPOSED PORTION OF FILM
5 m/m STEPS
30° BETWEEN STEPS
7 cms. RAD.
PULLEY 2 cm DIA.
MAX RAD OF WHEEL 7 CMS.
DIA OF PULLEY 2 CMS
12 SECTORS EACH 30°
DEPTH OF STEP 5 M/M
SEGMENT WHEEL (BRASS)

FIG. 5.

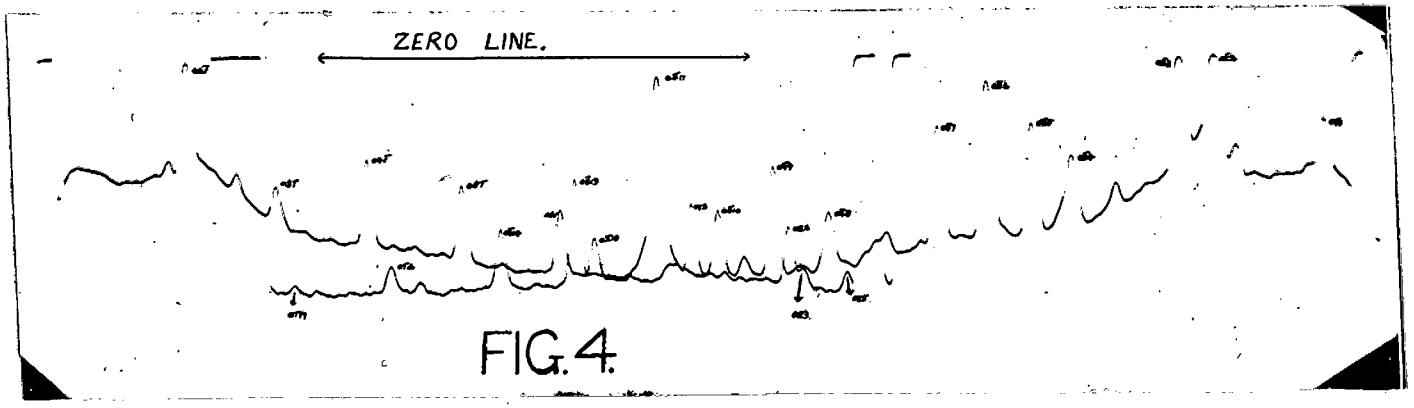
ZERO LINE.

FIG. 4.

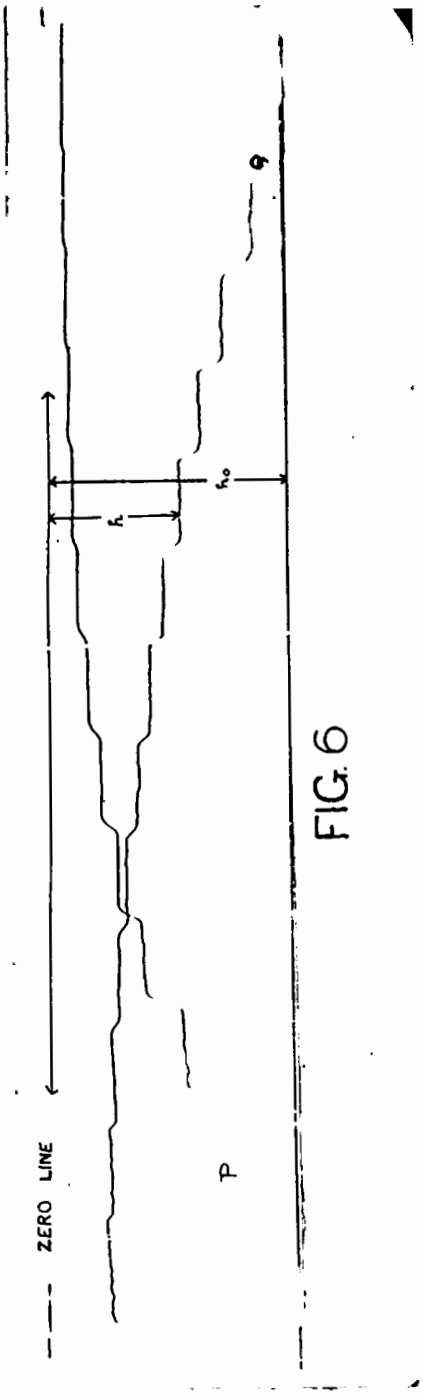

FIG. 6

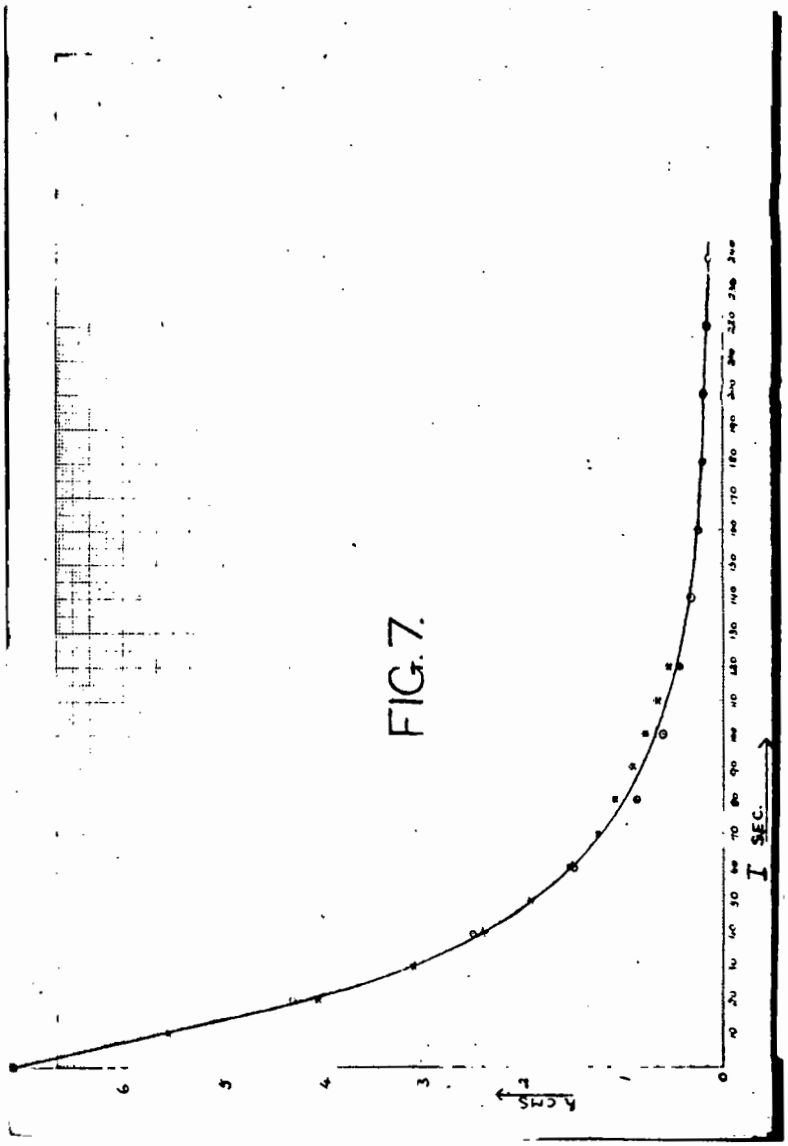

FIG. 7.

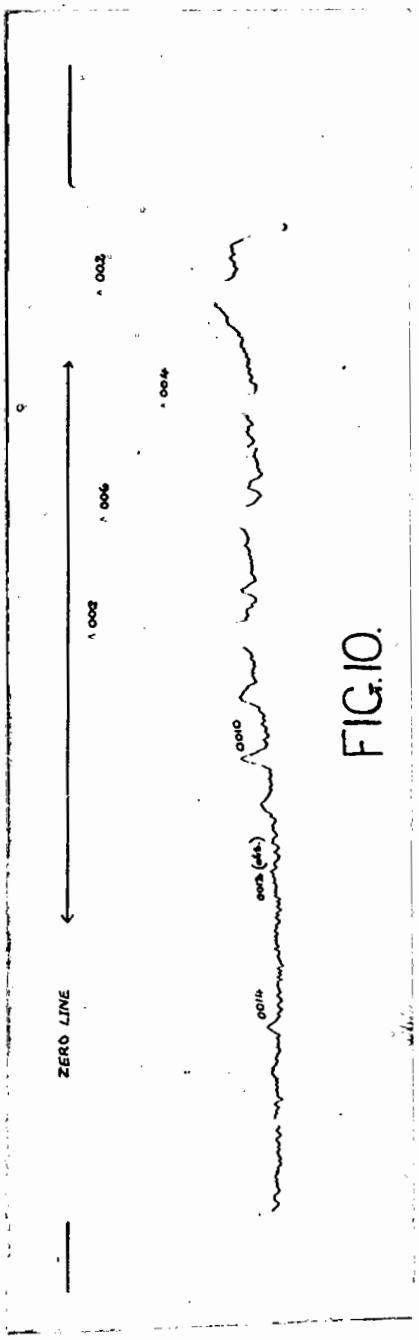

FIG.10.

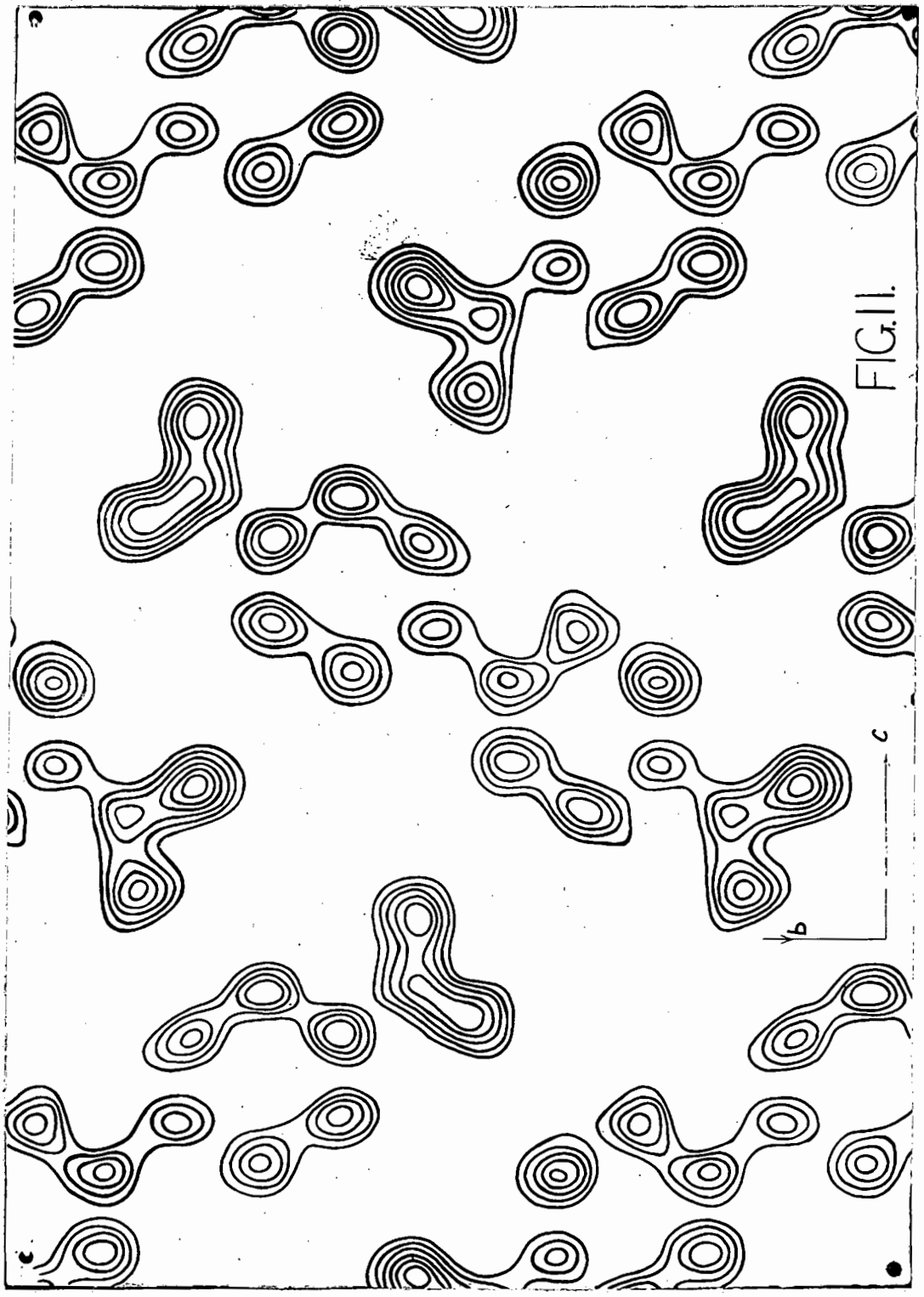

FIG. II.

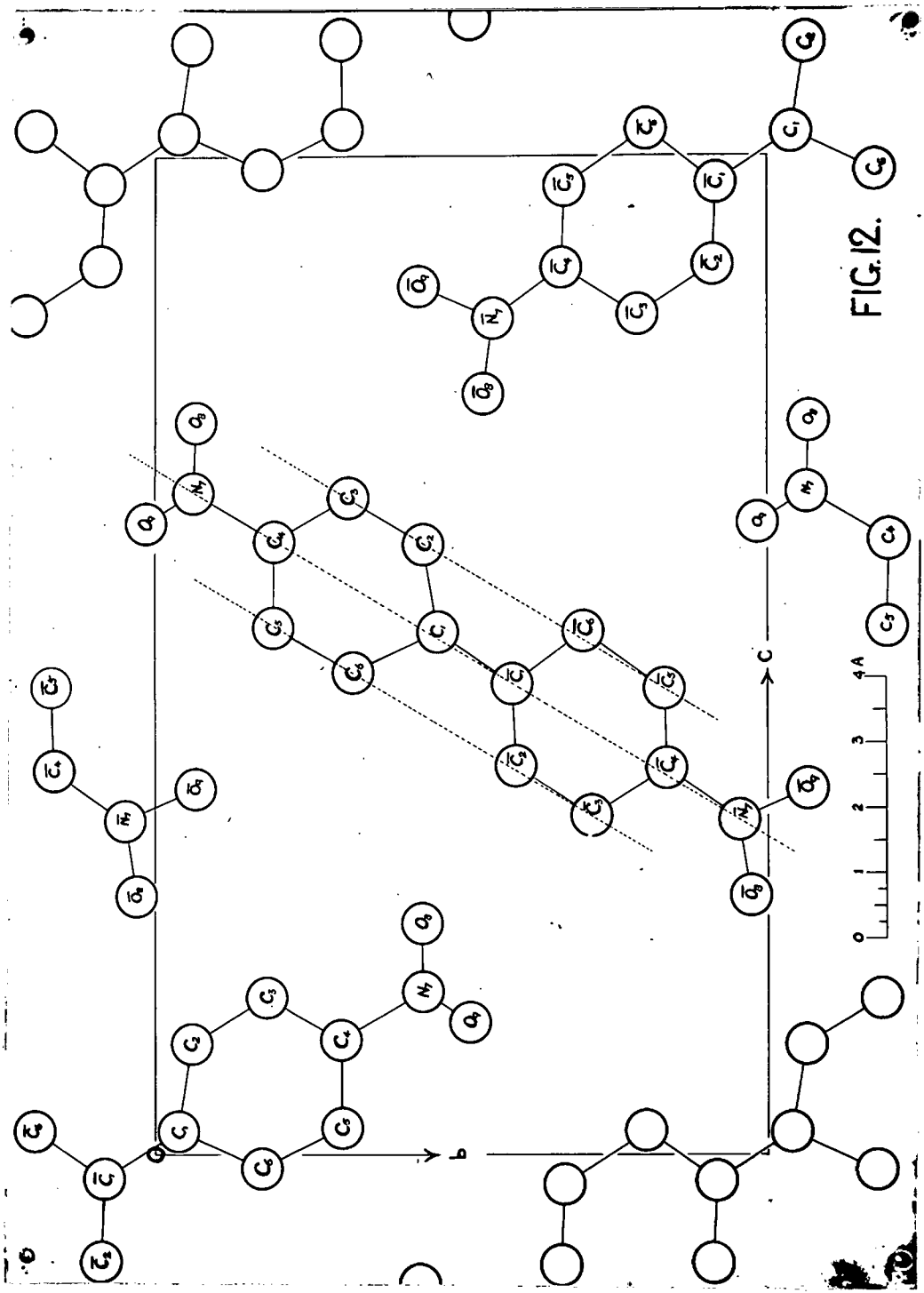

FIG. 12.

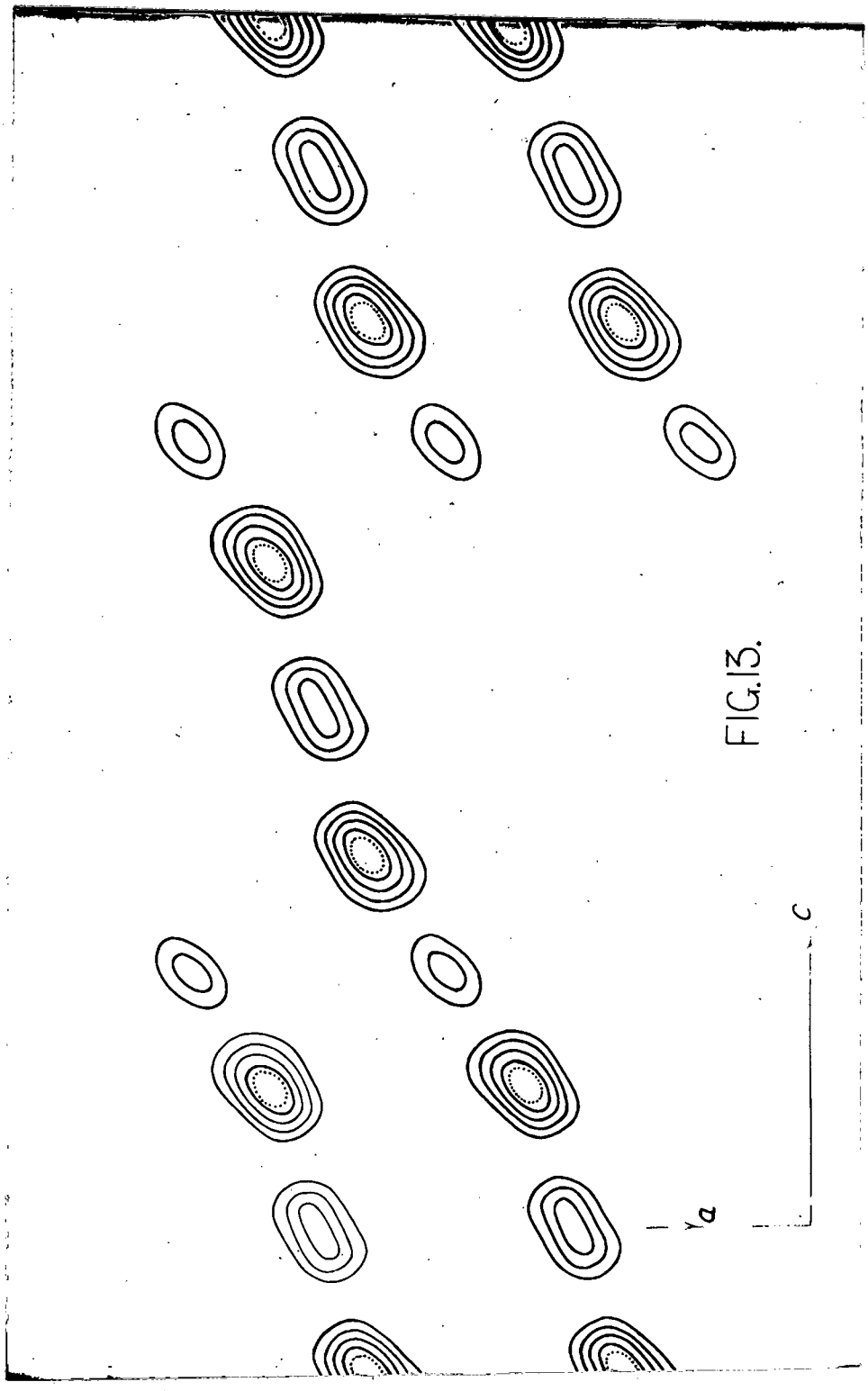

FIG. 13.

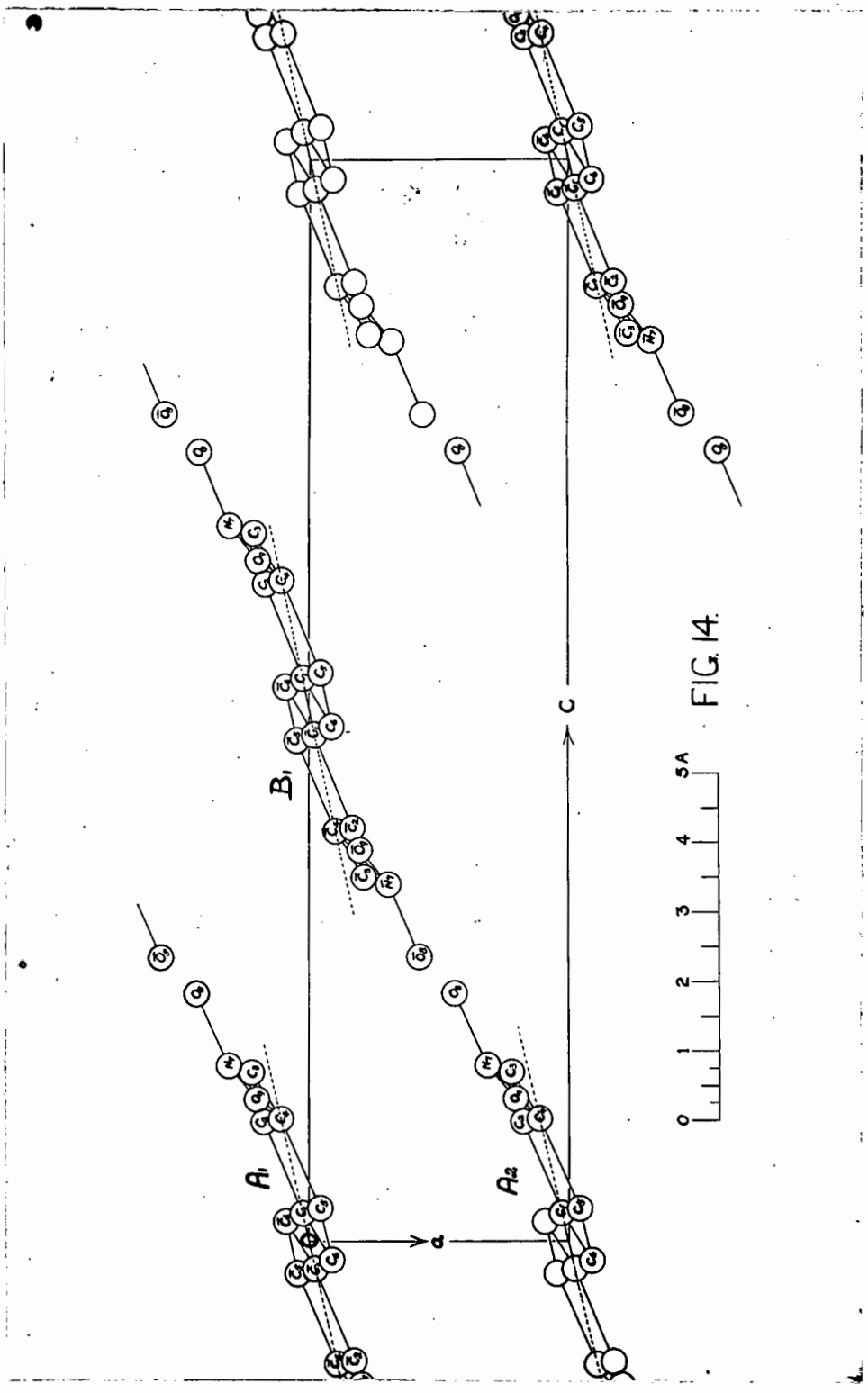

FIG. 14.

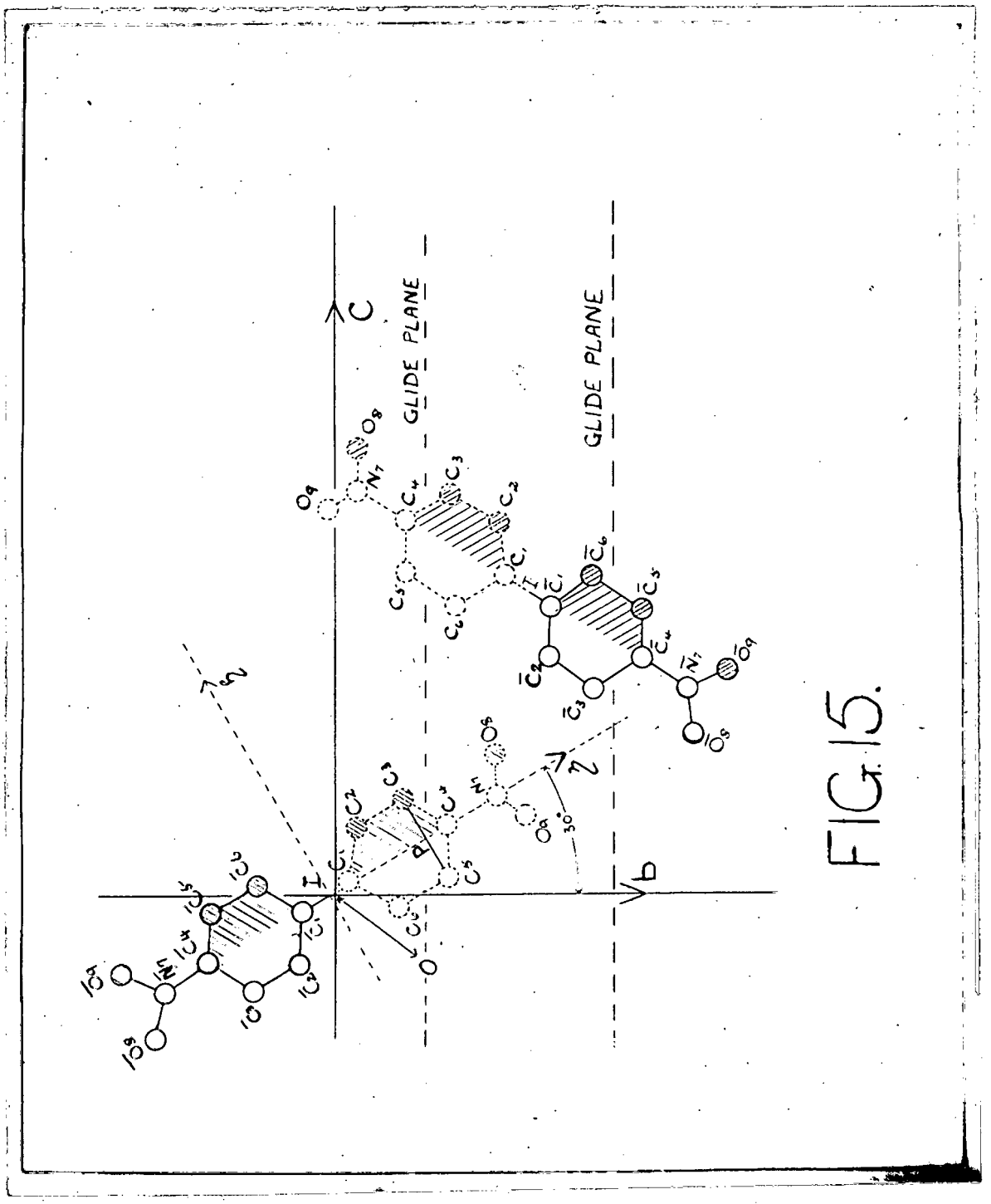

FIG. 15.

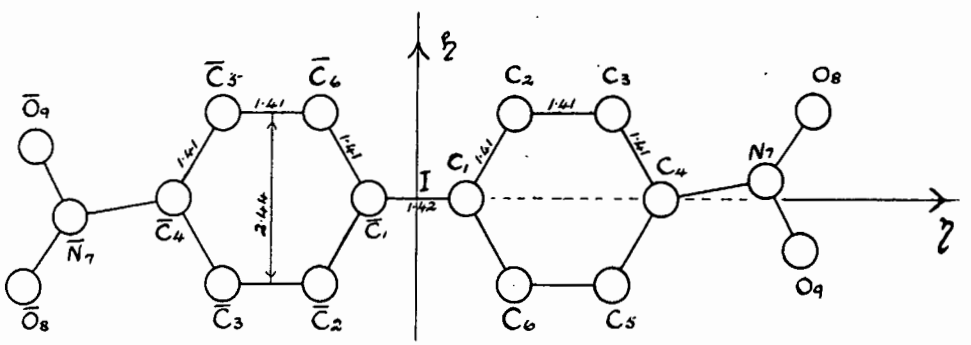

FIG. 16a.

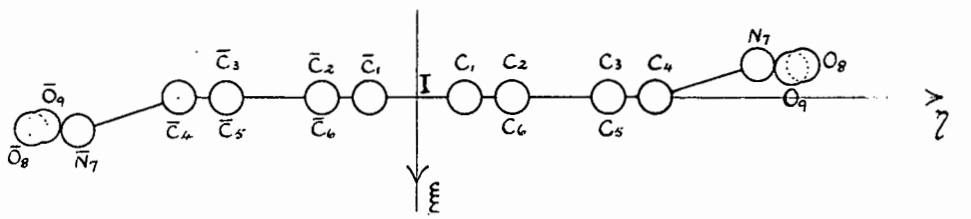

FIG. 16b.

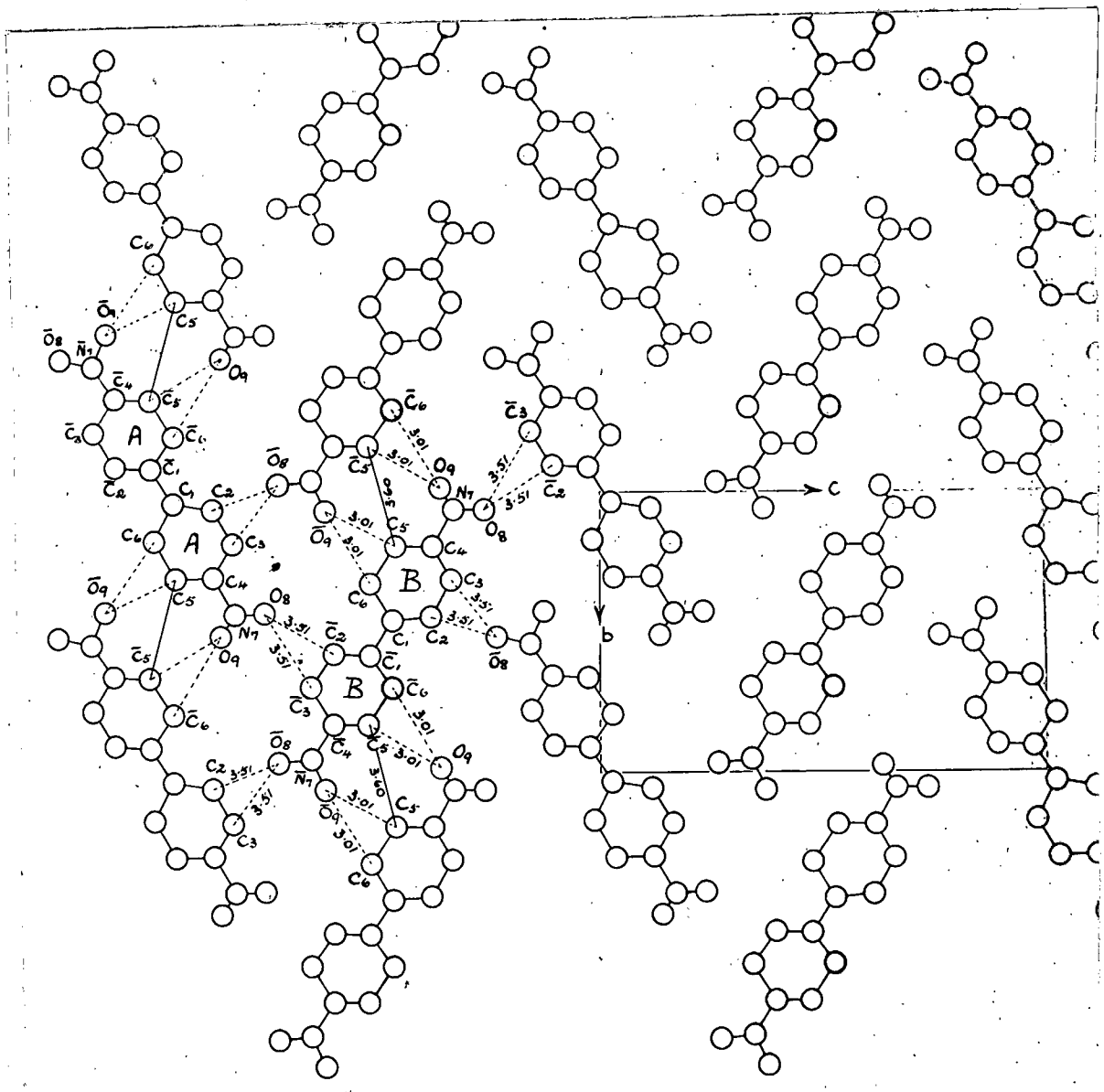

FIG. 17.

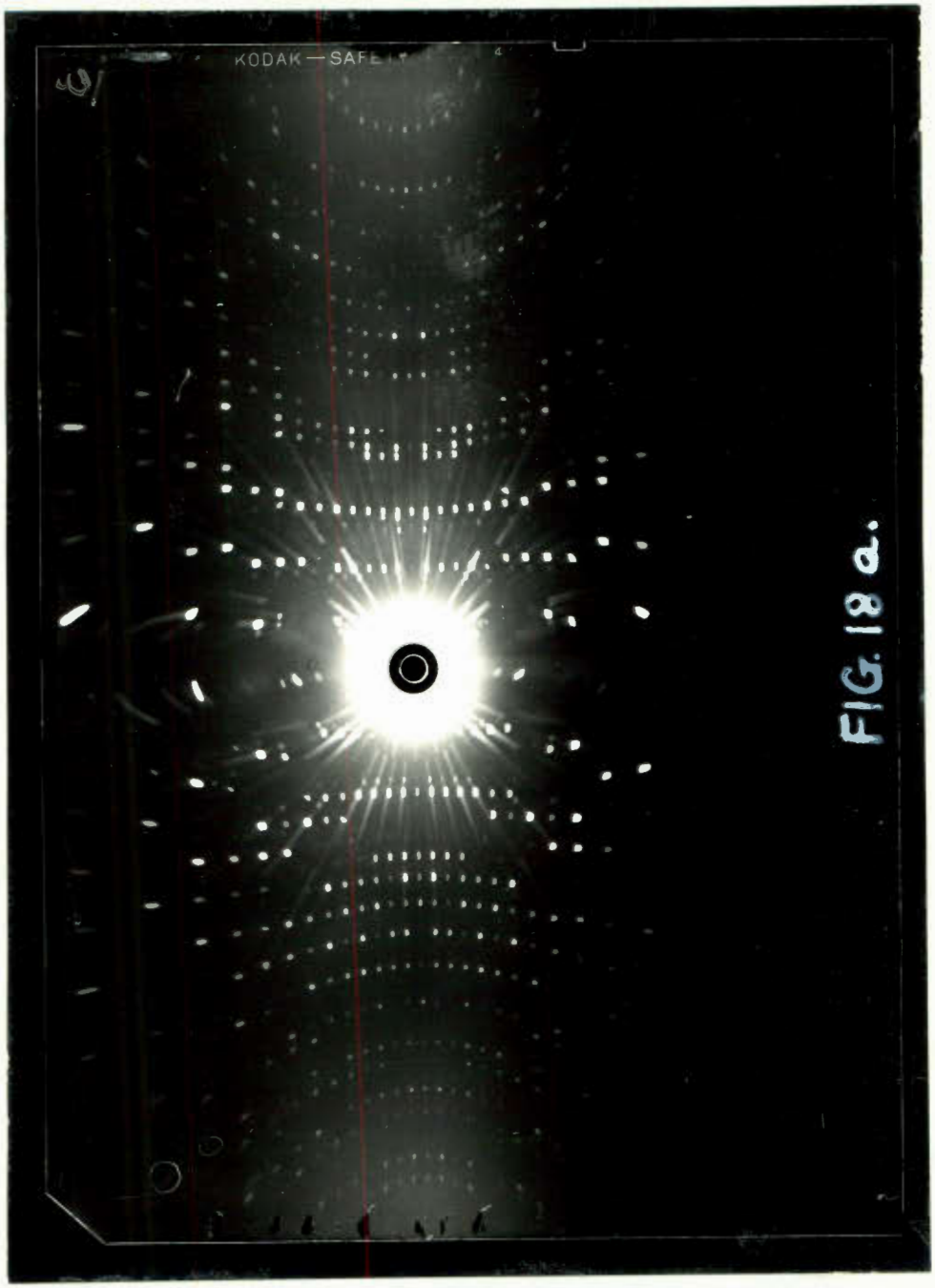

FIG. 18 a.

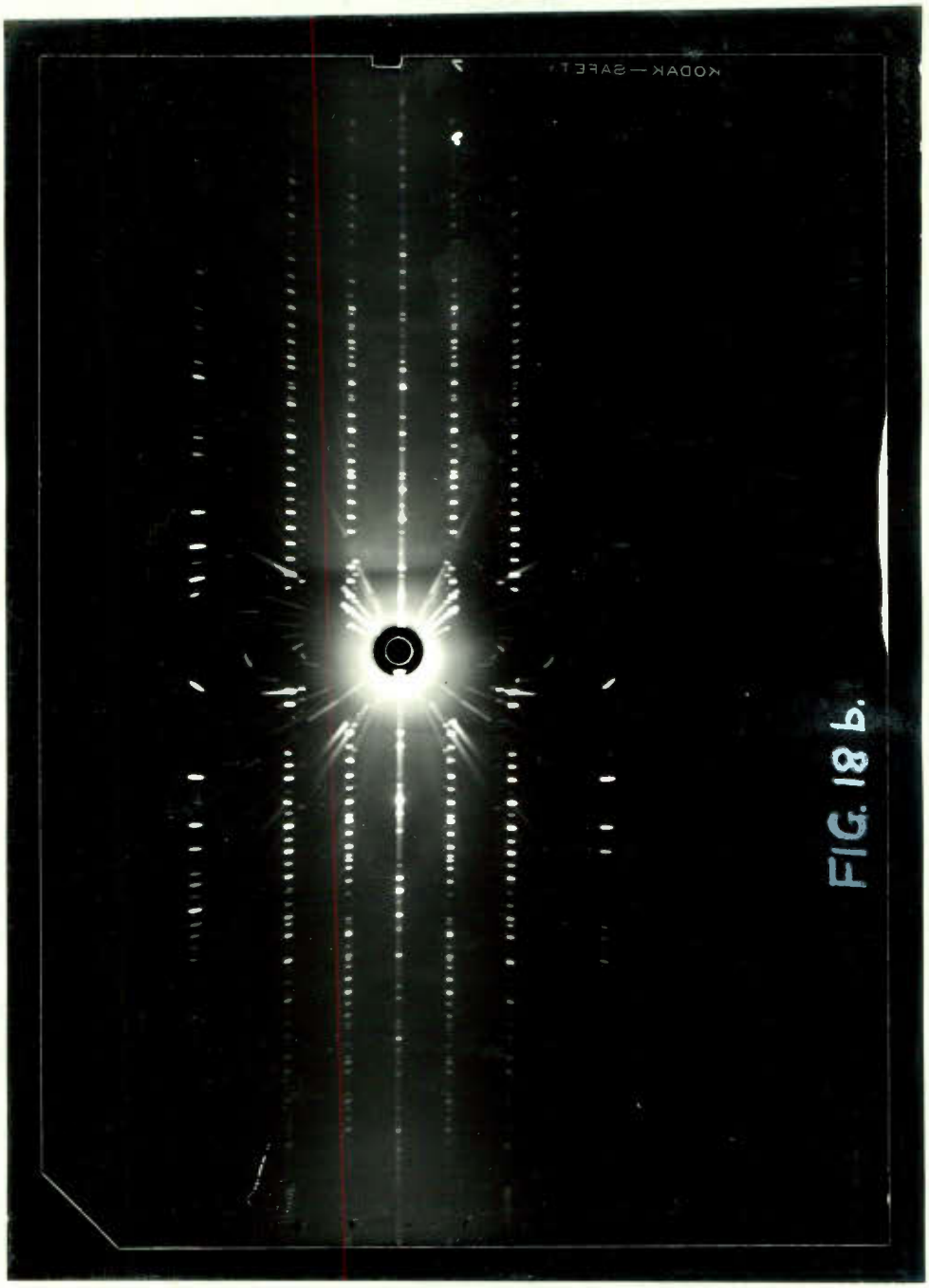

FIG. 18 b.

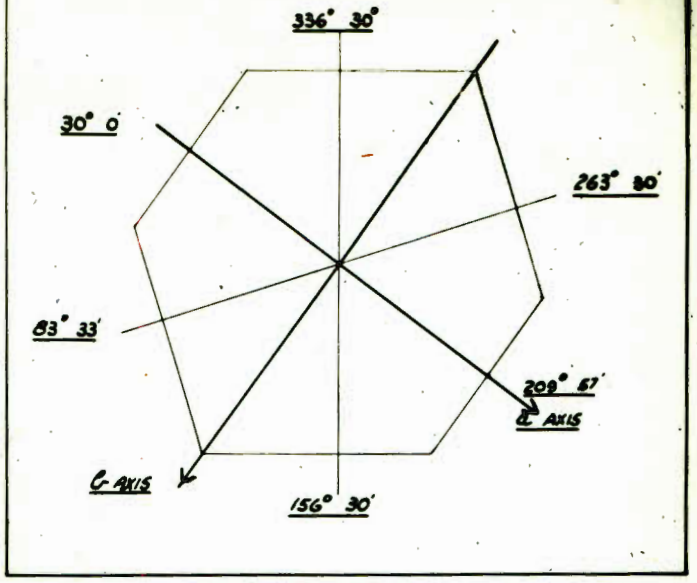

FIG. 19.

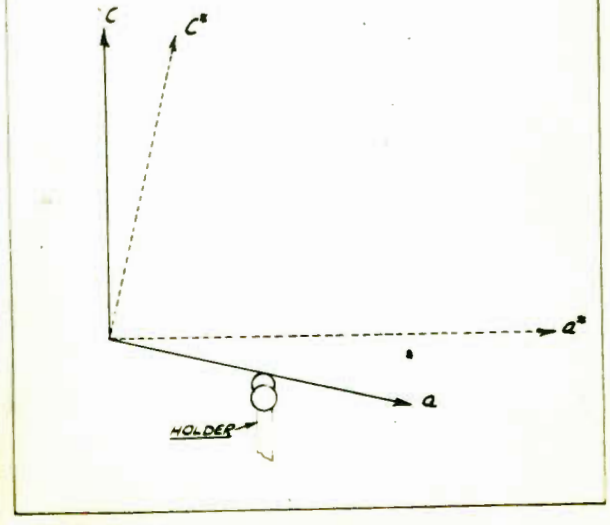

FIG. 20.

FIG. 21a.

FIG. 21b.